

\* \* \* \* \* STN Columbus \* \* \* \* \*

FILE 'HOME' ENTERED AT 15:10:14 ON 06 MAR 2009

=>

=> file registry

COST IN U.S. DOLLARS

SINCE FILE

TOTAL

ENTRY

SESSION

FULL ESTIMATED COST

0.22

0.22

FILE 'REGISTRY' ENTERED AT 15:10:28 ON 06 MAR 2009

USE IS SUBJECT TO THE TERMS OF YOUR STN CUSTOMER AGREEMENT.

PLEASE SEE "HELP USAGETERMS" FOR DETAILS.

COPYRIGHT (C) 2009 American Chemical Society (ACS)

Property values tagged with IC are from the ZIC/VINITI data file  
provided by InfoChem.

STRUCTURE FILE UPDATES: 4 MAR 2009 HIGHEST RN 1115640-24-8

DICTIONARY FILE UPDATES: 4 MAR 2009 HIGHEST RN 1115640-24-8

New CAS Information Use Policies, enter HELP USAGETERMS for details.

TSCA INFORMATION NOW CURRENT THROUGH January 9, 2009.

Please note that search-term pricing does apply when  
conducting SmartSELECT searches.

REGISTRY includes numerically searchable data for experimental and  
predicted properties as well as tags indicating availability of  
experimental property data in the original document. For information  
on property searching in REGISTRY, refer to:

<http://www.cas.org/support/stngen/stndoc/properties.html>

=> s 6674-22-2/cn

L1 0 6674-22-2/CN

=> s 6674-22-2/rn

L2 1 6674-22-2/RN

=> file caplus

COST IN U.S. DOLLARS

SINCE FILE

TOTAL

ENTRY

SESSION

FULL ESTIMATED COST

7.75

7.97

FILE 'CAPLUS' ENTERED AT 15:13:10 ON 06 MAR 2009

USE IS SUBJECT TO THE TERMS OF YOUR STN CUSTOMER AGREEMENT.

PLEASE SEE "HELP USAGETERMS" FOR DETAILS.

COPYRIGHT (C) 2009 AMERICAN CHEMICAL SOCIETY (ACS)

Copyright of the articles to which records in this database refer is  
held by the publishers listed in the PUBLISHER (PB) field (available  
for records published or updated in Chemical Abstracts after December  
26, 1996), unless otherwise indicated in the original publications.  
The CA Lexicon is the copyrighted intellectual property of the  
American Chemical Society and is provided to assist you in searching

databases on STN. Any dissemination, distribution, copying, or storing of this information, without the prior written consent of CAS, is strictly prohibited.

FILE COVERS 1907 - 6 Mar 2009 VOL 150 ISS 11  
FILE LAST UPDATED: 5 Mar 2009 (20090305/ED)

Caplus now includes complete International Patent Classification (IPC) reclassification data for the third quarter of 2008.

CAS Information Use Policies apply and are available at:

<http://www.cas.org/legal/infopolicy.html>

This file contains CAS Registry Numbers for easy and accurate substance identification.

=> s L2

L3 3786 L2

=> file registry

COST IN U.S. DOLLARS	SINCE FILE ENTRY	TOTAL SESSION
FULL ESTIMATED COST	0.50	8.47

FILE 'REGISTRY' ENTERED AT 15:13:28 ON 06 MAR 2009  
USE IS SUBJECT TO THE TERMS OF YOUR STN CUSTOMER AGREEMENT.  
PLEASE SEE "HELP USAGETERMS" FOR DETAILS.  
COPYRIGHT (C) 2009 American Chemical Society (ACS)

Property values tagged with IC are from the ZIC/VINITI data file provided by InfoChem.

STRUCTURE FILE UPDATES: 4 MAR 2009 HIGHEST RN 1115640-24-8  
DICTIONARY FILE UPDATES: 4 MAR 2009 HIGHEST RN 1115640-24-8

New CAS Information Use Policies, enter HELP USAGETERMS for details.

TSCA INFORMATION NOW CURRENT THROUGH January 9, 2009.

Please note that search-term pricing does apply when conducting SmartSELECT searches.

REGISTRY includes numerically searchable data for experimental and predicted properties as well as tags indicating availability of experimental property data in the original document. For information on property searching in REGISTRY, refer to:

<http://www.cas.org/support/stngen/stndoc/properties.html>

=> s 7320-37-8/rn

L4 1 7320-37-8/RN

=> d L4

L4 ANSWER 1 OF 1 REGISTRY COPYRIGHT 2009 ACS on STN  
RN \*\*\*7320-37-8\*\*\* REGISTRY  
ED Entered STN: 16 Nov 1984  
CN Oxirane, 2-tetradecyl- (CA INDEX NAME)  
OTHER CA INDEX NAMES:

CN Hexadecane, 1,2-epoxy- (6CI, 7CI, 8CI)  
 CN Oxirane, tetradecyl- (9CI)  
 OTHER NAMES:  
 CN 1,2-Epoxyhexadecane  
 CN 1,2-Epoxyhexadecene  
 CN 1,2-Hexadecene epoxide  
 CN 1,2-Hexadecylene oxide  
 CN 1-Hexadecene oxide  
 CN Cyracure UVR 6216  
 CN Hexadecylene oxide  
 CN Tetradecyloxirane  
 CN UVR 6216  
 CN Vikolox 16  
 DR 151284-10-5  
 MF C16 H32 O  
 CI COM  
 LC STN Files: ANABSTR, BEILSTEIN\*, BIOSIS, CA, CAPLUS, CASREACT,  
 CHEMCATS,  
 CHEMINFORMRX, CHEMLIST, CSCHEM, CSNB, HSDB\*, IFICDB, IFIPAT,  
 IFIUDB,  
 PIRA, PROMT, RTECS\*, SPECINFO, TOXCENTER, USPAT2, USPATFULL,  
 USPATOLD  
 (\*File contains numerically searchable property data)  
 Other Sources: EINECS\*\*, NDSL\*\*, TSCA\*\*  
 (\*\*Enter CHEMLIST File for up-to-date regulatory information)

/ Structure 1 in file .gra /

\*\*PROPERTY DATA AVAILABLE IN THE 'PROP' FORMAT\*\*

331 REFERENCES IN FILE CA (1907 TO DATE)  
 103 REFERENCES TO NON-SPECIFIC DERIVATIVES IN FILE CA  
 331 REFERENCES IN FILE CAPLUS (1907 TO DATE)

=> s 3001-72-7/rn  
 L5 1 3001-72-7/RN

=> d L5

L5 ANSWER 1 OF 1 REGISTRY COPYRIGHT 2009 ACS on STN  
 RN \*\*\*3001-72-7\*\*\* REGISTRY  
 ED Entered STN: 16 Nov 1984  
 CN Pyrrolo[1,2-a]pyrimidine, 2,3,4,6,7,8-hexahydro- (CA INDEX NAME)  
 OTHER NAMES:  
 CN 1,5-Diazabicyclo[4.3.0]non-5-ene  
 CN 1,5-Diazobicyclo[4.3.0]non-5-ene  
 CN 2,3,4,6,7,8-Hexahydropyrrolo[1,2-a]pyrimidine  
 CN DBN  
 CN DBN (heterocycle)  
 CN NBU  
 CN NSC 118106  
 DR 25986-32-7, 312727-86-9  
 MF C7 H12 N2  
 CI COM  
 LC STN Files: ANABSTR, BEILSTEIN\*, BIOSIS, CA, CAPLUS, CASREACT,

CHEMCATS,  
CHEMINFORMRX, CHEMLIST, CSCHEM, GMELIN\*, IFICDB, IFIPAT, IFIUDB,  
MEDLINE, MSDS-OHS, SPECINFO, SYNTHLINE, TOXCENTER, USPAT2,  
USPATFULL,  
USPATOLD  
(\*File contains numerically searchable property data)  
Other Sources: EINECS\*\*  
(\*\*Enter CHEMLIST File for up-to-date regulatory information)

/ Structure 2 in file .gra /

\*\*PROPERTY DATA AVAILABLE IN THE 'PROP' FORMAT\*\*

1055 REFERENCES IN FILE CA (1907 TO DATE)  
40 REFERENCES TO NON-SPECIFIC DERIVATIVES IN FILE CA  
1056 REFERENCES IN FILE CAPLUS (1907 TO DATE)

=> d L2

L2 ANSWER 1 OF 1 REGISTRY COPYRIGHT 2009 ACS on STN  
RN \*\*\*6674-22-2\*\*\* REGISTRY  
ED Entered STN: 16 Nov 1984  
CN Pyrimido[1,2-a]azepine, 2,3,4,6,7,8,9,10-octahydro- (CA INDEX  
NAME)  
OTHER NAMES:  
CN 1,8-Diaza-7-bicyclo[5.4.0]undecene  
CN 1,8-Diazabicyclo[5.4.0]undec-7-ene  
CN 1,8-Diazabicyclo[5.4.0]undecene-7  
CN 2,3,4,6,7,8,9,10-Octahydropyrimido[1,2-a]azepine  
CN Amicure DBUE  
CN Dabco DBU  
CN DBU  
CN NSC 111184  
CN NSC 230466  
CN Polycat DBU  
CN U-CAT SA 851  
DR 51301-56-5, 69722-76-5, 78995-63-8, 83329-50-4, 31171-04-7, 41015-  
70-7  
MF C9 H16 N2  
CI COM  
LC STN Files: ANABSTR, BEILSTEIN\*, BIOSIS, CA, CAPLUS, CASREACT,  
CHEMCATS,  
CHEMINFORMRX, CHEMLIST, CIN, CSCHEM, GMELIN\*, IFICDB, IFIPAT,  
IFIUDB,  
MEDLINE, MSDS-OHS, SPECINFO, TOXCENTER, USPAT2, USPATFULL,  
USPATOLD  
(\*File contains numerically searchable property data)  
Other Sources: DSL\*\*, EINECS\*\*, TSCA\*\*  
(\*\*Enter CHEMLIST File for up-to-date regulatory information)

/ Structure 3 in file .gra /

\*\*PROPERTY DATA AVAILABLE IN THE 'PROP' FORMAT\*\*

3773 REFERENCES IN FILE CA (1907 TO DATE)



147 REFERENCES TO NON-SPECIFIC DERIVATIVES IN FILE CA  
3786 REFERENCES IN FILE CAPLUS (1907 TO DATE)

=> d his

(FILE 'HOME' ENTERED AT 15:10:14 ON 06 MAR 2009)

FILE 'REGISTRY' ENTERED AT 15:10:28 ON 06 MAR 2009

L1 0 S 6674-22-2/CN

L2 1 S 6674-22-2/RN

FILE 'CAPLUS' ENTERED AT 15:13:10 ON 06 MAR 2009

L3 3786 S L2

FILE 'REGISTRY' ENTERED AT 15:13:28 ON 06 MAR 2009

L4 1 S 7320-37-8/RN

L5 1 S 3001-72-7/RN

=> s triethylene (w) diamine

3806 TRIETHYLENE

438598 DIAMINE

76 DIAMINES

438598 DIAMINE

(DIAMINE OR DIAMINES)

L6 98 TRIETHYLENE (W) DIAMINE

=> s 280-57-9/rn

L7 1 280-57-9/RN

=> d L7

L7 ANSWER 1 OF 1 REGISTRY COPYRIGHT 2009 ACS on STN

RN \*\*\*280-57-9\*\*\* REGISTRY

ED Entered STN: 16 Nov 1984

CN 1,4-Diazabicyclo[2.2.2]octane (CA INDEX NAME)

OTHER NAMES:

CN 1,4-Ethylenepiperazine

CN 33LV

CN A 33

CN Activator 105E

CN Bicyclo[2.2.2]-1,4-diazaoctane

CN D 33LV

CN Dabco

CN Dabco 33LV

CN Dabco 3LV

CN DABCO Crystal

CN Dabco Crystalline

CN Dabco L 1202

CN Dabco S 25

CN Jeffcat TD 100

CN Kaolizer 31

CN L 33

CN L 33E

CN LC 96003

CN LV 33

CN Minico L 1020

CN N,N'-endo-Ethylenepiperazine

CN Niax A 33

CN NSC 56362

CN PC CAT TD 33  
 CN PC-TD  
 CN Polycat 33LV  
 CN TD 100  
 CN TED  
 CN TEDA  
 CN Teda L 33  
 CN Tegamine 33  
 CN Tego Amine  
 CN Texacat TD 100  
 CN Texacat TD 33  
 CN Thancat TD 33  
 CN Thancat TD 33A  
 CN Toral SM 2  
 CN Toyocat L 33  
 CN Toyocat TEDA L 33  
 CN Triethylenediamine  
 DR 903524-95-8, 165724-47-0, 23790-33-2, 101484-19-9, 150605-01-9,  
 88935-43-7, 203072-11-1, 309955-09-7  
 MF C6 H12 N2  
 CI COM, RPS  
 LC STN Files: AGRICOLA, ANABSTR, AQUIRE, BEILSTEIN\*, BIOSIS,  
 BIOTECHNO, CA,  
 CAPLUS, CASREACT, CBNB, CHEMCATS, CHEMINFORMRX, CHEMLIST, CIN,  
 CSCHEM,  
 CSNB, DETHERM\*, EMBASE, ENCOMPLIT, ENCOMPLIT2, ENCOMPPAT,  
 ENCOMPPAT2,  
 GMELIN\*, HSDB\*, IFICDB, IFIPAT, IFIUDB, MEDLINE, MRCK\*, MSDS-OHS,  
 PIRA,  
 PROMT, RTECS\*, SPECINFO, SYNTHLINE, TOXCENTER, ULIDAT, USPAT2,  
 USPATFULL, USPATOLD  
 (\*File contains numerically searchable property data)  
 Other Sources: DSL\*\*, EINECS\*\*, TSCA\*\*  
 (\*\*Enter CHEMLIST File for up-to-date regulatory information)

/ Structure 4 in file .gra /

\*\*PROPERTY DATA AVAILABLE IN THE 'PROP' FORMAT\*\*

6376 REFERENCES IN FILE CA (1907 TO DATE)  
 301 REFERENCES TO NON-SPECIFIC DERIVATIVES IN FILE CA  
 6392 REFERENCES IN FILE CAPLUS (1907 TO DATE)

=> d his

(FILE 'HOME' ENTERED AT 15:10:14 ON 06 MAR 2009)

FILE 'REGISTRY' ENTERED AT 15:10:28 ON 06 MAR 2009

L1 0 S 6674-22-2/CN  
 L2 1 S 6674-22-2/RN

FILE 'CAPLUS' ENTERED AT 15:13:10 ON 06 MAR 2009

L3 3786 S L2

FILE 'REGISTRY' ENTERED AT 15:13:28 ON 06 MAR 2009

L4 1 S 7320-37-8/RN  
 L5 1 S 3001-72-7/RN

L6 98 S TRIETHYLENE (W) DIAMINE  
L7 1 S 280-57-9/RN

=> file caplus uspatfull

COST IN U.S. DOLLARS

SINCE FILE

TOTAL

ENTRY

SESSION

FULL ESTIMATED COST

21.78

30.25

FILE 'CAPLUS' ENTERED AT 15:16:58 ON 06 MAR 2009

USE IS SUBJECT TO THE TERMS OF YOUR STN CUSTOMER AGREEMENT.

PLEASE SEE "HELP USAGETERMS" FOR DETAILS.

COPYRIGHT (C) 2009 AMERICAN CHEMICAL SOCIETY (ACS)

FILE 'USPATFULL' ENTERED AT 15:16:58 ON 06 MAR 2009

CA INDEXING COPYRIGHT (C) 2009 AMERICAN CHEMICAL SOCIETY (ACS)

=> s (L2 OR L5 OR L7) AND L4

L8 4 (L2 OR L5 OR L7) AND L4

=> d L8 1-4 ti ibib

L8 ANSWER 1 OF 4 CAPLUS COPYRIGHT 2009 ACS on STN

TI Hydrocarbon desulfurization with mercaptan removal by treatment  
with

alicyclic tertiary amines and nucleophilic acceptors

ACCESSION NUMBER: 2005:1027004 CAPLUS <<LOGINID::20090306>>

DOCUMENT NUMBER: 143:328922

TITLE: Hydrocarbon desulfurization with mercaptan  
removal by

treatment with alicyclic tertiary amines and  
nucleophilic acceptors

INVENTOR(S): Schield, John A.; Cappel, Weldon John

PATENT ASSIGNEE(S): Baker Hughes Incorporated, USA

SOURCE: PCT Int. Appl., 23 pp.

CODEN: PIXXD2

DOCUMENT TYPE: Patent

LANGUAGE: English

FAMILY ACC. NUM. COUNT: 1

PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
-----	----	-----	-----	-----
WO 2005087899	A1	20050922	WO 2004-US4011	
20040211				
W:	AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW			
RW:	BW, GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW, AM, AZ, BY, KG, KZ, MD, RU, TJ, TM, AT, BE, BG, CH, CY, CZ, DE, DK,			

EE,  
                  ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI,  
SK,  
                  TR, BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN,  
TD, TG  
          CA 2554548                  A1          20050922          CA 2004-2554548  
20040211  
          EP 1713885                  A1          20061025          EP 2004-710238  
20040211  
          R:  AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE, MC,  
PT,  
                  IE, SI, FI, RO, CY, TR, BG, CZ, EE, HU, SK  
          US 20070142244              A1          20070621          US 2006-588341  
20060803  
PRIORITY APPLN. INFO.:                                  WO 2004-US4011          W  
20040211  
OTHER SOURCE(S):                  MARPAT 143:328922  
REFERENCE COUNT:                  5          THERE ARE 5 CITED REFERENCES AVAILABLE  
FOR THIS  
                                  RECORD. ALL CITATIONS AVAILABLE IN THE RE  
FORMAT

L8  ANSWER 2 OF 4  CAPLUS  COPYRIGHT 2009 ACS on STN  
TI  Study of the structure-reactivity relationships in the  
photoinitiated  
      cationic polymerization of epoxide monomers  
ACCESSION NUMBER:          1998:808928  CAPLUS <<LOGINID::20090306>>  
DOCUMENT NUMBER:          130:182793  
TITLE:                    Study of the structure-reactivity relationships  
in the  
                          photoinitiated cationic polymerization of  
epoxide  
                          monomers  
AUTHOR(S):                Crivello, James V.; Linzer, Volker  
CORPORATE SOURCE:         Polymer Synthesis Center, Department of  
Chemistry,  
                          Rensselaer Polytechnic Institute, Troy, NY,  
                          12180-3590, USA  
SOURCE:                   Polimery (Warsaw) (1998), 43(11/12), 661-672  
                          CODEN: POLIA4; ISSN: 0032-2725  
PUBLISHER:                Instytut Chemii Przemyslowej  
DOCUMENT TYPE:             Journal  
LANGUAGE:                 English  
REFERENCE COUNT:          21          THERE ARE 21 CITED REFERENCES AVAILABLE  
FOR THIS  
                          RECORD. ALL CITATIONS AVAILABLE IN THE RE  
FORMAT

L8  ANSWER 3 OF 4  CAPLUS  COPYRIGHT 2009 ACS on STN  
TI  Grease-compatible, hydrolytically stable encapsulant compositions  
for use  
      in signal transmission devices  
ACCESSION NUMBER:          1991:103808  CAPLUS <<LOGINID::20090306>>  
DOCUMENT NUMBER:          114:103808  
ORIGINAL REFERENCE NO.:  114:17695a,17698a  
TITLE:                    Grease-compatible, hydrolytically stable  
encapsulant  
                          compositions for use in signal transmission  
devices  
INVENTOR(S):              Croft, Thomas S.; Haugen, Hartwick A.

PATENT ASSIGNEE(S): Minnesota Mining and Manufacturing Co., USA  
 SOURCE: Eur. Pat. Appl., 26 pp.  
 CODEN: EPXXDW  
 DOCUMENT TYPE: Patent  
 LANGUAGE: English  
 FAMILY ACC. NUM. COUNT: 1  
 PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
EP 372747	A2	19900613	EP 1989-312078	
19891121				
EP 372747	A3	19901010		
EP 372747	B1	19950823		
R: AT, CH, DE, ES, FR, GB, IT, LI, SE				
AU 8945338	A	19900531	AU 1989-45338	
19891120				
AU 620662	B2	19920220		
ES 2076218	T3	19951101	ES 1989-312078	
19891121				
CA 2003781	A1	19900525	CA 1989-2003781	
19891124				
CA 2003781	C	19990216		
JP 02212580	A	19900823	JP 1989-306376	
19891124				
JP 2772075	B2	19980702		
KR 135973	B1	19980424	KR 1989-17080	
19891124				
BR 8905961	A	19900619	BR 1989-5961	
19891127				
PRIORITY APPLN. INFO.:			US 1988-274337	A
19881125				

L8 ANSWER 4 OF 4 USPATFULL on STN  
 TI Encapsulant compositions for use in signal transmission devices  
 ACCESSION NUMBER: 91:5171 USPATFULL <<LOGINID::20090306>>  
 TITLE: Encapsulant compositions for use in signal  
 transmission

INVENTOR(S): Croft, Thomas S., Austin, TX, United States  
 Haugen, Hartwick, Austin, TX, United States  
 PATENT ASSIGNEE(S): Minnesota Mining and Manufacturing, St. Paul,  
 MN,  
 United States (U.S. corporation)

	NUMBER	KIND	DATE
PATENT INFORMATION:	US 4985475		19910115
APPLICATION INFO.:	US 1988-274337		19881125 (7)
RELATED APPLN. INFO.:	Continuation-in-part of Ser. No. US 1987-19295, filed on 9 Mar 1987, now patented, Pat. No. US 4857563		
DOCUMENT TYPE:	Utility		
FILE SEGMENT:	Granted		
PRIMARY EXAMINER:	Schofer, Joseph L.		
ASSISTANT EXAMINER:	Mulcahy, Peter D.		
LEGAL REPRESENTATIVE:	Sell, D. M., Lilly, J. V.		
NUMBER OF CLAIMS:	17		
EXEMPLARY CLAIM:	1		

LINE COUNT: 1302  
CAS INDEXING IS AVAILABLE FOR THIS PATENT.

=> d 1-4 hit, bib

L8 ANSWER 1 OF 4 CAPLUS COPYRIGHT 2009 ACS on STN  
IT \*\*\*280-57-9\*\*\* , 1,4-Diazabicyclo[2.2.2]octane \*\*\*3001-72-7\*\*\*

,  
1,5-Diazabicyclo[4.3.0]non-5-ene \*\*\*6674-22-2\*\*\* ,  
1,8-Diazabicyclo[5.4.0]undec-7-ene  
RL: CPS (Chemical process); PEP (Physical, engineering or chemical  
process); PROC (Process)

(hydrocarbon desulfurization with mercaptan removal by treatment  
with  
alicyclic tertiary amines and nucleophilic acceptors)

IT 463-73-0D, Chloroformic acid, compds. 2817-45-0D, Phosphoramidic  
acid,  
compds. \*\*\*7320-37-8\*\*\* , 1,2-Epoxyhexadecane 19270-07-6D,  
Cyanofomic acid, compds.

RL: CPS (Chemical process); PEP (Physical, engineering or chemical  
process); PROC (Process)  
(nucleophilic acceptors; hydrocarbon desulfurization with

mercaptan  
removal by treatment with alicyclic tertiary amines and  
nucleophilic  
acceptors)

AN 2005:1027004 CAPLUS <<LOGINID::20090306>>

DN 143:328922

TI Hydrocarbon desulfurization with mercaptan removal by treatment  
with

alicyclic tertiary amines and nucleophilic acceptors

IN Schield, John A.; Cappel, Weldon John

PA Baker Hughes Incorporated, USA

SO PCT Int. Appl., 23 pp.

CODEN: PIXXD2

DT Patent

LA English

FAN.CNT 1

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
------------	------	------	-----------------	------

PI WO 2005087899	A1	20050922	WO 2004-US4011	
20040211				
CH,	W:	AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA,		
GD,		CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB,		
LC,		GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ,		
NI,		LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA,		
SY,		NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL,		
ZW		TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM,		
AZ,	RW:	BW, GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW, AM,		
EE,		BY, KG, KZ, MD, RU, TJ, TM, AT, BE, BG, CH, CY, CZ, DE, DK,		

ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI,  
 SK,  
 TR, BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN,  
 TD, TG  
 CA 2554548 A1 20050922 CA 2004-2554548  
 20040211  
 EP 1713885 A1 20061025 EP 2004-710238  
 20040211  
 R: AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE, MC,  
 PT,  
 IE, SI, FI, RO, CY, TR, BG, CZ, EE, HU, SK  
 US 20070142244 A1 20070621 US 2006-588341  
 20060803  
 PRAI WO 2004-US4011 W 20040211  
 OS MARPAT 143:328922  
 RE.CNT 5 THERE ARE 5 CITED REFERENCES AVAILABLE FOR THIS RECORD  
 ALL CITATIONS AVAILABLE IN THE RE FORMAT

L8 ANSWER 2 OF 4 CAPLUS COPYRIGHT 2009 ACS on STN  
 IT 108-87-2, 1-Methylcyclohexane 291-64-5, Cycloheptane \*\*\*6674-  
 22-2\*\*\*  
 , 1,8-Diazabicyclo[5.4.0]undec-7-ene 10353-53-4, 1,2-Epoxyhex-5-  
 ene  
 55334-42-4, 1,2-Dibromododecane 85721-25-1  
 RL: RCT (Reactant); RACT (Reactant or reagent)  
 (reactant in monomer prepn.; structure effect on kinetics of  
 photoinitiated cationic polymn. of epoxides)  
 IT 285-67-6, Epoxycyclopentane 286-20-4, 7-Oxabicyclo[4.1.0]heptane  
 286-62-4, Epoxycyclooctane 1436-34-6 1464-53-5, 2,2'-Bioxirane  
 1502-29-0, cis-Epoxycyclododecane 1686-14-2, .alpha.-Pinene oxide  
 1758-33-4, cis-2,3-Epoxybutane 2404-44-6 2426-07-5 2855-19-8  
 2984-50-1 3234-28-4 4683-60-7, trans-Epoxycyclododecane  
 \*\*\*7320-37-8\*\*\* 21490-63-1, trans-2,3-Epoxybutane  
 RL: PRP (Properties); RCT (Reactant); RACT (Reactant or reagent)  
 (structure effect on kinetics of photoinitiated cationic polymn.  
 of  
 epoxides)  
 AN 1998:808928 CAPLUS <<LOGINID::20090306>>  
 DN 130:182793  
 TI Study of the structure-reactivity relationships in the  
 photoinitiated  
 cationic polymerization of epoxide monomers  
 AU Crivello, James V.; Linzer, Volker  
 CS Polymer Synthesis Center, Department of Chemistry, Rensselaer  
 Polytechnic  
 Institute, Troy, NY, 12180-3590, USA  
 SO Polimery (Warsaw) (1998), 43(11/12), 661-672  
 CODEN: POLIA4; ISSN: 0032-2725  
 PB Instytut Chemii Przemyslowej  
 DT Journal  
 LA English  
 RE.CNT 21 THERE ARE 21 CITED REFERENCES AVAILABLE FOR THIS RECORD  
 ALL CITATIONS AVAILABLE IN THE RE FORMAT

L8 ANSWER 3 OF 4 CAPLUS COPYRIGHT 2009 ACS on STN  
 IT 101-34-8, Flexricin P 8 112-75-4 1191-43-1, 1,6-Hexanedithiol  
 3319-31-1 3489-28-9, 1,9-Nonanedithiol \*\*\*6674-22-2\*\*\*  
 \*\*\*7320-37-8\*\*\* , Vikolox 16 9044-17-1, Indopol H 100 10482-  
 56-1  
 25085-98-7, ERL 4221 25155-23-1, Trixylenyl phosphate 25231-21-

4

25266-02-8, PA-18 26616-47-7, ERL 4234 37226-48-5, Araldite  
 53564-35-5, Escopol R020 81647-91-8, Paol 40 132325-11-2,  
 FuelSaver  
 RL: USES (Uses)  
 (encapsulation compns. contg., grease-compatible, hydrolytically  
 stable, for signal transmission devices)  
 AN 1991:103808 CAPLUS <<LOGINID::20090306>>  
 DN 114:103808  
 OREF 114:17695a,17698a  
 TI Grease-compatible, hydrolytically stable encapsulant compositions  
 for use  
 in signal transmission devices  
 IN Croft, Thomas S.; Haugen, Hartwick A.  
 PA Minnesota Mining and Manufacturing Co., USA  
 SO Eur. Pat. Appl., 26 pp.  
 CODEN: EPXXDW  
 DT Patent  
 LA English  
 FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
	-----	----	-----	-----	
PI	EP 372747	A2	19900613	EP 1989-312078	
19891121					
	EP 372747	A3	19901010		
	EP 372747	B1	19950823		
	R: AT, CH, DE, ES, FR, GB, IT, LI, SE				
	AU 8945338	A	19900531	AU 1989-45338	
19891120					
	AU 620662	B2	19920220		
	ES 2076218	T3	19951101	ES 1989-312078	
19891121					
	CA 2003781	A1	19900525	CA 1989-2003781	
19891124					
	CA 2003781	C	19990216		
	JP 02212580	A	19900823	JP 1989-306376	
19891124					
	JP 2772075	B2	19980702		
	KR 135973	B1	19980424	KR 1989-17080	
19891124					
	BR 8905961	A	19900619	BR 1989-5961	
19891127					
PRAI	US 1988-274337	A	19881125		

L8 ANSWER 4 OF 4 USPATFULL on STN  
 IT 101-34-8, Flexricin P 8 112-75-4 1191-43-1, 1,6-Hexanedithiol  
 3319-31-1 3489-28-9, 1,9-Nonanedithiol \*\*\*6674-22-2\*\*\*  
 \*\*\*7320-37-8\*\*\* , Vikolox 16 9044-17-1, Indopol H 100  
 10482-56-1  
 25085-98-7, ERL 4221 25155-23-1, Trixylenyl phosphate 25231-  
 21-4  
 25266-02-8, PA-18 26616-47-7, ERL 4234 37226-48-5, Araldite  
 53564-35-5, Escopol R020 81647-91-8, Paol 40 132325-11-2,  
 FuelSaver

(encapsulation compns. contg., grease-compatible, hydrolytically  
 stable, for signal transmission devices)  
 AN 91:5171 USPATFULL <<LOGINID::20090306>>  
 TI Encapsulant compositions for use in signal transmission devices  
 IN Croft, Thomas S., Austin, TX, United States



Haugen, Hartwick, Austin, TX, United States  
 PA Minnesota Mining and Manufacturing, St. Paul, MN, United States  
 (U.S. corporation)  
 PI US 4985475 19910115  
 AI US 1988-274337 19881125 (7)  
 RLI Continuation-in-part of Ser. No. US 1987-19295, filed on 9 Mar  
 1987, now patented, Pat. No. US 4857563  
 DT Utility  
 FS Granted  
 EXNAM Primary Examiner: Schofer, Joseph L.; Assistant Examiner:  
 Mulcahy, Peter  
 D.  
 LREP Sell, D. M., Lilly, J. V.  
 CLMN Number of Claims: 17  
 ECL Exemplary Claim: 1  
 DRWN No Drawings  
 LN.CNT 1302  
 CAS INDEXING IS AVAILABLE FOR THIS PATENT.

=> s (L2 OR L5 OR L7) AND thiolysis  
 L9 3 (L2 OR L5 OR L7) AND THIOLYSIS

=> d L9 1-3 hit, ibib

L9 ANSWER 1 OF 3 CAPLUS COPYRIGHT 2009 ACS on STN  
 ST siloxane tetrahydro hydrogen rich prepn alcoholysis dihalosilane  
 pyridine  
 complex; alkylthio disilathiane tetrahydro hydrogen rich prepn  
 \*\*\*thiolysis\*\*\* dihalosilane complex; process prepn hydrogen  
 rich  
 siloxane disilathiane alcoholysis \*\*\*thiolysis\*\*\* dihalosilane  
 IT Amines, preparation  
 RL: RCT (Reactant); SPN (Synthetic preparation); PREP  
 (Preparation); RACT  
 (Reactant or reagent)  
 (complexes, silicon; process for prepn. of hydrogen-rich  
 1,1,3,3-tetrahydrodisiloxanes and -disilathianes by alcoholysis  
 and  
 \*\*\*thiolysis\*\*\* of dihalosilane pyridine complexes)  
 IT Siloxanes (nonpolymeric)  
 RL: SPN (Synthetic preparation); PREP (Preparation)  
 (disiloxanes, hydrogen-rich; process for prepn. of hydrogen-rich  
 1,1,3,3-tetrahydrodisiloxanes and -disilathianes by alcoholysis  
 and  
 \*\*\*thiolysis\*\*\* of dihalosilane pyridine complexes)  
 IT Alcoholysis  
 (process for prepn. of hydrogen-rich 1,1,3,3-  
 tetrahydrodisiloxanes and  
 -disilathianes by alcoholysis and \*\*\*thiolysis\*\*\* of  
 dihalosilane  
 pyridine complexes)  
 IT Group IVA element compounds  
 Group VIA element compounds  
 RL: SPN (Synthetic preparation); PREP (Preparation)  
 (silathianes, 1,3-disilathianes; process for prepn. of hydrogen-  
 rich  
 1,1,3,3-tetrahydrodisiloxanes and -disilathianes by alcoholysis

and  
 \*\*\*thiolysis\*\*\* of dihalosilane pyridine complexes)

IT Alcohols, reactions  
 Thiols, reactions  
 RL: RCT (Reactant); RACT (Reactant or reagent)  
 (tertiary; process for prepn. of hydrogen-rich  
 1,1,3,3-tetrahydrodisiloxanes and -disilathianes by alcoholysis

and  
 \*\*\*thiolysis\*\*\* of dihalosilane pyridine complexes)

IT Solvolysis  
 ( \*\*\*thiolysis\*\*\* ; process for prepn. of hydrogen-rich  
 1,1,3,3-tetrahydrodisiloxanes and -disilathianes by alcoholysis

and  
 \*\*\*thiolysis\*\*\* of dihalosilane pyridine complexes)

IT 953776-96-0P  
 RL: PRPH (Prophetic); RCT (Reactant); SPN (Synthetic preparation);  
 PREP  
 (Preparation); RACT (Reactant or reagent)  
 (process for prepn. of hydrogen-rich 1,1,3,3-  
 tetrahydrodisiloxanes and  
 -disilathianes by alcoholysis and \*\*\*thiolysis\*\*\* of  
 dihalosilane  
 pyridine complexes)

IT 75-65-0, tert-Butanol, reactions 75-66-1, tert-Butylmercaptan  
 75-85-4,  
 tert-Amyl alcohol 77-74-7 100-43-6, 4-Vinylpyridine 108-47-4,  
 2,4-Dimethylpyridine 108-89-4, 4-Methylpyridine 108-99-6,  
 3-Methylpyridine 109-06-8, 2-Methylpyridine 110-86-1, Pyridine,  
 reactions 536-75-4, 4-Ethylpyridine 590-36-3 590-67-0 594-  
 83-2  
 595-41-5 597-05-7 597-49-9 597-93-3 598-01-6 626-55-1,  
 3-Bromopyridine 690-37-9 702-81-8, 3-Methyl-1-adamantanol  
 768-95-6,  
 Tricyclo[3.3.1.1<sup>3,7</sup>]decan-1-ol 880-49-9, 3-Isopropyl-1-  
 adamantanol  
 1122-58-3 1462-03-9, 1-Methylcyclopentanol 1569-44-4 1569-46-  
 6  
 1604-02-0 1633-97-2 1639-01-6 1639-03-8 1679-09-0 1940-  
 18-7,  
 1-Ethylcyclohexanol 3742-85-6 3761-94-2 3978-81-2,  
 4-tert-Butylpyridine 4109-96-0, Dichlorosilane 5445-24-9  
 5827-80-5  
 17257-32-8 20534-58-1, Bicyclo[2.2.2]octan-1-ol 23511-76-4  
 71897-97-7 74356-31-3 87383-23-1 91337-12-1 108836-86-8  
 116436-16-9 124547-52-0 186365-89-9 189394-12-5 200403-44-7  
 RL: RCT (Reactant); RACT (Reactant or reagent)  
 (process for prepn. of hydrogen-rich 1,1,3,3-  
 tetrahydrodisiloxanes and  
 -disilathianes by alcoholysis and \*\*\*thiolysis\*\*\* of  
 dihalosilane  
 pyridine complexes)

IT 75-50-3, Trimethylamine, reactions 79-55-0,  
 1,2,2,6,6-Pentamethylpiperidine 100-76-5, 1-Azabicyclo[2.2.2]  
 octane  
 102-82-9, Tributylamine 121-44-8, Triethylamine, reactions  
 \*\*\*280-57-9\*\*\* , 1,4-Diazabicyclo[2.2.2]octane \*\*\*3001-72-7\*\*\*  
 ,  
 1,5-Diazabicyclo[4.3.0]non-5-ene 4458-31-5 5807-14-7,  
 1,5,7-Triazabicyclo[4.4.0]dec-5-ene \*\*\*6674-22-2\*\*\* ,  
 1,8-Diazabicyclo[5.4.0]undec-7-ene 20634-92-8 84030-20-6,

7-Methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene  
 RL: RGT (Reagent); RACT (Reactant or reagent)  
 (process for prepn. of hydrogen-rich 1,1,3,3-tetrahydrodisiloxanes and  
 -disilathianes by alcoholysis and \*\*\*thiolysis\*\*\* of  
 dihalosilane  
 pyridine complexes)  
 IT 1002788-53-5P 1002788-54-6P 1002788-55-7P  
 RL: SPN (Synthetic preparation); PREP (Preparation)  
 (process for prepn. of hydrogen-rich 1,1,3,3-tetrahydrodisiloxanes and  
 -disilathianes by alcoholysis and \*\*\*thiolysis\*\*\* of  
 dihalosilane  
 pyridine complexes)  
 ACCESSION NUMBER: 2008:90945 CAPLUS <<LOGINID::20090306>>  
 DOCUMENT NUMBER: 148:168827  
 TITLE: Process for preparation of novel hydrogen-rich  
 1,1,3,3-tetrahydro-1,3-disiloxanes and  
 1,3-disilathianes as precursors for  
 hydrosilylation,  
 polymerization and material modifiers  
 INVENTOR(S): Fester, Gerrit; Roewer, Gerhard; Kroke, Edwin  
 PATENT ASSIGNEE(S): Technische Universitaet Bergakademie Freiberg,  
 Germany  
 SOURCE: PCT Int. Appl., 20pp.  
 CODEN: PIXXD2  
 DOCUMENT TYPE: Patent  
 LANGUAGE: German  
 FAMILY ACC. NUM. COUNT: 1  
 PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
WO 2008009680	A1	20080124	WO 2007-EP57379	
20070717				
W:	AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ,			
CA,	CH, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES,			
FI,	GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE,			
KG,	KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD,			
ME,	MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PG, PH,			
PL,	PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, SV, SY, TJ, TM,			
TN,	TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW			
RW:	AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU,			
IE,	IS, IT, LT, LU, LV, MC, MT, NL, PL, PT, RO, SE, SI, SK, TR,			
BF,	BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG,			
BW,	GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW, AM,			
AZ,	BY, KG, KZ, MD, RU, TJ, TM			
PRIORITY APPLN. INFO.:			DE 2006-102006034336A	
20060717				

OTHER SOURCE(S): CASREACT 148:168827; MARPAT 148:168827  
REFERENCE COUNT: 1 THERE ARE 1 CITED REFERENCES AVAILABLE  
FOR THIS  
RECORD. ALL CITATIONS AVAILABLE IN THE RE  
FORMAT

L9 ANSWER 2 OF 3 CAPLUS COPYRIGHT 2009 ACS on STN  
TI Improved process for preparation of hydrosilanes containing alkoxy,  
amino  
and thiolato groups by alcoholysis, aminolysis and  
\*\*\*thiolysis\*\*\* of  
halosilanes in the presence of tertiary amine bases  
ST silane hydrosilane alkoxy amino thiolate prepn process; alcoholysis  
aminolysis \*\*\*thiolysis\*\*\* chlorosilane tertiary amine base  
process  
IT Silanes  
RL: SPN (Synthetic preparation); TEM (Technical or engineered  
material  
use); PREP (Preparation); USES (Uses)  
(alkoxy, hydrosilanes; process for prepn. of hydrosilanes contg.  
alkoxy, amino and thioether substituents by alcoholysis,  
aminolysis and  
\*\*\*thiolysis\*\*\* of halosilanes in presence of tertiary amine  
base)  
IT Silanes  
RL: RCT (Reactant); RACT (Reactant or reagent)  
(halosilanes, hydrosilanes; process for prepn. of hydrosilanes  
contg.  
alkoxy, amino and thioether substituents by alcoholysis,  
aminolysis and  
\*\*\*thiolysis\*\*\* of halosilanes in presence of tertiary amine  
base)  
IT Thioethers  
RL: SPN (Synthetic preparation); TEM (Technical or engineered  
material  
use); PREP (Preparation); USES (Uses)  
(hydrosilane; process for prepn. of hydrosilanes contg. alkoxy,  
amino  
and thioether substituents by alcoholysis, aminolysis and  
\*\*\*thiolysis\*\*\* of halosilanes in presence of tertiary amine  
base)  
IT Silanes  
RL: RCT (Reactant); SPN (Synthetic preparation); TEM (Technical or  
engineered material use); PREP (Preparation); RACT (Reactant or  
reagent);  
USES (Uses)  
(hydrosilanes; process for prepn. of hydrosilanes contg. alkoxy,  
amino  
and thioether substituents by alcoholysis, aminolysis and  
\*\*\*thiolysis\*\*\* of halosilanes in presence of tertiary amine  
base)  
IT Silazanes  
RL: SPN (Synthetic preparation); TEM (Technical or engineered  
material  
use); PREP (Preparation); USES (Uses)  
(hydrosilanes; process for prepn. of hydrosilanes contg. alkoxy,  
amino  
and thioether substituents by alcoholysis, aminolysis and  
\*\*\*thiolysis\*\*\* of halosilanes in presence of tertiary amine  
base)

IT 56-24-6 64-17-5, Ethanol, reactions 67-56-1, Methanol, reactions  
 67-63-0, Isopropanol, reactions 71-23-8, 1-Propanol, reactions  
 71-36-3, 1-Butanol, reactions 71-41-0, 1-Pentanol, reactions  
 75-08-1,  
 Ethanethiol 75-33-2, 2-Propanethiol 76-84-6, Triphenylmethanol  
 76-87-9 78-83-1, Isobutanol, reactions 96-41-3, Cyclopentanol  
 98-85-1 100-51-6, Benzenemethanol, reactions 103-49-1,  
 Dibenzylamine  
 107-03-9, 1-Propanethiol 107-18-6, Allyl alcohol, reactions  
 107-19-7,  
 2-Propyn-1-ol 108-18-9, Diisopropylamine 108-89-4, 4-  
 Methylpyridine  
 108-93-0, Cyclohexanol, reactions 108-95-2, Phenol, reactions  
 108-98-5, Benzenethiol, reactions 109-79-5, 1-Butanethiol 109-  
 89-7,  
 Diethylamine, reactions 110-89-4, Piperidine, reactions 110-96-  
 3,  
 Diisobutylamine 111-92-2, Dibutylamine 115-19-5 123-51-3  
 123-75-1,  
 Pyrrolidine, reactions 142-84-7, Dipropylamine 513-42-8 513-  
 44-0  
 583-59-5, 2-Methylcyclohexanol 597-52-4, Triethylsilanol 598-  
 32-3,  
 3-Buten-2-ol 627-27-0, 3-Buten-1-ol 764-01-2, 2-Butyn-1-ol  
 791-31-1  
 894-08-6 927-74-2, 3-Butyn-1-ol 994-32-1 1066-40-6,  
 Trimethylsilanol  
 1067-96-5 1067-97-6 1189-31-7 1529-27-7, Triphenylgermanol  
 1529-35-7 1569-69-3, Cyclohexanethiol 1679-07-8,  
 Cyclopentanethiol  
 2028-63-9, 3-Butyn-2-ol 2216-51-5, (-)-Menthol 2622-89-1,  
 Borinic  
 acid, diphenyl- 2628-46-8 3695-77-0 4109-96-0, Dichlorosilane  
 4237-48-3 4426-31-7 4453-82-1 4631-63-4 5337-72-4 5906-  
 79-6  
 6117-91-5, 2-Buten-1-ol 6300-99-8 13061-97-7 13121-70-5  
 15356-60-2, (+)-Menthol 17546-98-4, Trimethylplumbanol 17687-  
 73-9  
 17687-74-0 17877-23-5 17888-60-7 18388-85-7 18547-88-1,  
 Tricyclohexylsilanol 26819-05-6 36633-36-0 52102-16-6  
 55999-97-8  
 56889-90-8, Tri-tert-butylsilanol 66952-11-2 82490-11-7  
 96383-35-6  
 98156-23-1 104503-69-7 118978-84-0 134178-80-6 171503-79-0  
 228092-38-4 317374-14-4 718642-35-4 855637-46-6 860704-01-4  
 952755-22-5 952755-23-6 952755-24-7 952755-25-8 952755-26-9  
 952755-27-0 952755-28-1 952755-29-2 952755-30-5 952755-31-6  
 952755-32-7 952755-33-8 952755-34-9  
 RL: RCT (Reactant); RACT (Reactant or reagent)  
 (process for prepn. of hydrosilanes contg. alkoxy, amino and  
 thioether  
 substituents by alcoholysis, aminolysis and \*\*\*thiolysis\*\*\*  
 of  
 halosilanes in presence of tertiary amine base)  
 IT 952755-20-3P 952755-21-4P 953776-96-0P  
 RL: RCT (Reactant); SPN (Synthetic preparation); PREP  
 (Preparation); RACT  
 (Reactant or reagent)  
 (process for prepn. of hydrosilanes contg. alkoxy, amino and

thioether  
substituents by alcoholysis, aminolysis and \*\*\*thiolysis\*\*\*  
of  
halosilanes in presence of tertiary amine base)  
IT 75-50-3, Trimethylamine, reactions 110-86-1, Pyridine, reactions  
121-44-8, Triethylamine, reactions \*\*\*280-57-9\*\*\* ,  
1,4-Diazabicyclo[2.2.2]octane 289-95-2, Pyrimidine 290-37-9,  
Pyrazine  
\*\*\*3001-72-7\*\*\* 4458-31-5 \*\*\*6674-22-2\*\*\* , DBU 20634-  
92-8  
RL: RGT (Reagent); RACT (Reactant or reagent)  
(process for prepn. of hydrosilanes contg. alkoxy, amino and  
thioether  
substituents by alcoholysis, aminolysis and \*\*\*thiolysis\*\*\*  
of  
halosilanes in presence of tertiary amine base)  
IT 1507-99-9P 2487-90-3P 5314-52-3P 6675-79-2P 18165-68-9P  
18165-77-0P 20114-49-2P 27804-64-4P 38442-21-6P,  
Diphenoxysilane  
149578-93-8P 220214-19-7P 859765-44-9P 952755-06-5P 952755-  
07-6P  
952755-08-7P 952755-09-8P 952755-10-1P 952755-11-2P 952755-  
12-3P  
952755-13-4P 952755-14-5P 952755-15-6P 952755-16-7P 952755-  
17-8P  
952755-18-9P 952755-19-0P  
RL: SPN (Synthetic preparation); TEM (Technical or engineered  
material  
use); PREP (Preparation); USES (Uses)  
(process for prepn. of hydrosilanes contg. alkoxy, amino and  
thioether  
substituents by alcoholysis, aminolysis and \*\*\*thiolysis\*\*\*  
of  
halosilanes in presence of tertiary amine base)  
ACCESSION NUMBER: 2007:1204421 CAPLUS <<LOGINID::20090306>>  
DOCUMENT NUMBER: 147:486546  
TITLE: Improved process for preparation of  
hydrosilanes  
containing alkoxy, amino and thiolato groups by  
alcoholysis, aminolysis and \*\*\*thiolysis\*\*\*  
of  
halosilanes in the presence of tertiary amine  
bases  
INVENTOR(S): Fester, Gerrit; Roewer, Gerhard; Kroke, Edwin  
PATENT ASSIGNEE(S): Technische Universitaet Bergakademie Freiberg,  
Germany  
SOURCE: PCT Int. Appl., 43pp.  
CODEN: PIXXD2  
DOCUMENT TYPE: Patent  
LANGUAGE: German  
FAMILY ACC. NUM. COUNT: 1  
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
-----	----	-----	-----	-----
WO 2007118474	A2	20071025	WO 2007-DE724	
20070419				
WO 2007118474	A3	20071221		
W:	AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ,			

CA,  
 GB, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI,  
 KM, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG,  
 MK, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, MG,  
 RO, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT,  
 TT, RS, RU, SC, SD, SE, SG, SK, SL, SM, SV, SY, TJ, TM, TN, TR,  
 TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW  
 IE, RW: AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU,  
 BF, IS, IT, LT, LU, LV, MC, MT, NL, PL, PT, RO, SE, SI, SK, TR,  
 BW, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG,  
 AZ, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW, AM,  
 BY, KG, KZ, MD, RU, TJ, TM, AP, EA, EP, OA

DE 102006019016 A1 20071025 DE 2006-102006019016  
 20060419  
 PRIORITY APPLN. INFO.: DE 2006-102006019016A  
 20060419 DE 2006-102006034335A

20060717  
 OTHER SOURCE(S): CASREACT 147:486546; MARPAT 147:486546

L9 ANSWER 3 OF 3 CAPLUS COPYRIGHT 2009 ACS on STN  
 IT Solvolysis catalysts  
 ( \*\*\*thiolysis\*\*\* ; compn. for depilation contg. complexes of  
 aluminum or zinc complexes with thioglycolic acid)  
 IT 102-71-6, Triethanolamine, biological studies \*\*\*280-57-9\*\*\* ,  
 1,4-Diazabicyclo[2.2.2]octane \*\*\*6674-22-2\*\*\* ,  
 1,8-Diazabicyclo[5.4.0]undec-7-ene  
 RL: CAT (Catalyst use); COS (Cosmetic use); BIOL (Biological  
 study); USES  
 (Uses)  
 (compn. for depilation contg. complexes of aluminum or zinc  
 complexes  
 with thioglycolic acid)

ACCESSION NUMBER: 2006:1354152 CAPLUS <<LOGINID::20090306>>  
 DOCUMENT NUMBER: 146:106772  
 TITLE: Composition for depilation containing complexes  
 of

aluminum or zinc complexes with thioglycolic  
 acid

INVENTOR(S): Marte, Walter; Meyer, Martin; Dutler, Hans;  
 Zimmermann, Michael

PATENT ASSIGNEE(S): Tex-A-Tec AG, Switz.  
 SOURCE: PCT Int. Appl., 47pp.  
 CODEN: PIXXD2

DOCUMENT TYPE: Patent  
 LANGUAGE: German

FAMILY ACC. NUM. COUNT: 2  
 PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
-----	----	-----	-----	-----

```

-----
WO 2006136441      A1      20061228      WO 2006-EP6080
20060623
W:  AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA,
CH,
    CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB,
GD,
    GE, GH, GM, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN,
KP,
    KR, KZ, LA, LC, LK, LR, LS, LT, LU, LV, LY, MA, MD, MG, MK,
MN,
    MW, MX, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RS,
RU,
    SC, SD, SE, SG, SK, SL, SM, SY, TJ, TM, TN, TR, TT, TZ, UA,
UG,
    US, UZ, VC, VN, ZA, ZM, ZW
RW: AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU,
IE,
    IS, IT, LT, LU, LV, MC, NL, PL, PT, RO, SE, SI, SK, TR, BF,
BJ,
    CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG, BW,
GH,
    GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW, AM, AZ,
BY,
    KG, KZ, MD, RU, TJ, TM
EP 1736207      A1      20061227      EP 2005-13593
20050623
R:  AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU,
IE,
    IS, IT, LI, LT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR, AL,
BA,
    HR, LV, MK, YU
EP 1779899      A1      20070502      EP 2005-26090
20051130
R:  AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU,
IE,
    IS, IT, LI, LT, LU, LV, MC, NL, PL, PT, RO, SE, SI, SK, TR,
AL,
    BA, HR, MK, YU
EP 1917073      A1      20080507      EP 2006-762166
20060623
R:  AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU,
IE,
    IS, IT, LI, LT, LU, LV, MC, NL, PL, PT, RO, SE, SI, SK, TR
PRIORITY APPLN. INFO.:      EP 2005-13593      A
20050623
                                EP 2005-26090      A
20051130
                                WO 2006-EP6080      W
20060623
REFERENCE COUNT:      7      THERE ARE 7 CITED REFERENCES AVAILABLE
FOR THIS
                                RECORD. ALL CITATIONS AVAILABLE IN THE RE
FORMAT

```

```

=> s (L2 OR L5 OR L7) AND epoxide
L10      489 (L2 OR L5 OR L7) AND EPOXIDE

```

```

=> s L10 and (mercaptan OR thiol)

```



L11 85 L10 AND (MERCAPTAN OR THIOL)

=> d L11 1-85 ti

L11 ANSWER 1 OF 85 CAPLUS COPYRIGHT 2009 ACS on STN

TI Process for preparation of substituted 2-aminoethylsulfonic acids

L11 ANSWER 2 OF 85 CAPLUS COPYRIGHT 2009 ACS on STN

TI Tertiary amines as highly efficient catalysts in the ring-opening reactions of \*\*\*epoxides\*\*\* with amines or \*\*\*thiols\*\*\* in

H2O:

expeditious approach to .beta.-amino alcohols and .beta.-aminothioethers

L11 ANSWER 3 OF 85 CAPLUS COPYRIGHT 2009 ACS on STN

TI Hydrocarbon desulfurization with \*\*\*mercaptan\*\*\* removal by treatment with alicyclic tertiary amines and nucleophilic acceptors

L11 ANSWER 4 OF 85 CAPLUS COPYRIGHT 2009 ACS on STN

TI Artificial neural network for predicting the toxicity of organic molecules

L11 ANSWER 5 OF 85 CAPLUS COPYRIGHT 2009 ACS on STN

TI Regio- and stereospecific synthesis of (O-TIPS)-protected 2-hydroxyalkylmercaptans from \*\*\*epoxides\*\*\* and triisopropylsilanethiol

L11 ANSWER 6 OF 85 CAPLUS COPYRIGHT 2009 ACS on STN

TI Reaction of 1,2-dioxetanes with heteroatom nucleophiles: adduct formation by nucleophilic attack at the peroxide bond

L11 ANSWER 7 OF 85 CAPLUS COPYRIGHT 2009 ACS on STN

TI Polymercaptan-fused ring amine catalysts for curing epoxy resins

L11 ANSWER 8 OF 85 USPATFULL on STN

TI ORGANOMETALLIC COMPOSITIONS AND COATING COMPOSITIONS

L11 ANSWER 9 OF 85 USPATFULL on STN

TI Thiourethane Compositions and Processes for Making and Using Same

L11 ANSWER 10 OF 85 USPATFULL on STN

TI SEQUENTIAL ANALYSIS OF BIOLOGICAL SAMPLES

L11 ANSWER 11 OF 85 USPATFULL on STN

TI SEQUENTIAL ANALYSIS OF BIOLOGICAL SAMPLES

L11 ANSWER 12 OF 85 USPATFULL on STN

TI Method of producing flexible laminates

L11 ANSWER 13 OF 85 USPATFULL on STN

TI Synthesis and Applications of 2-Oxo-4-Methylthiobutyric Acid, Its Salts and Its Derivatives

L11 ANSWER 14 OF 85 USPATFULL on STN

TI FLUORESCENT BIOMOLECULE LABELING REAGENTS

L11 ANSWER 15 OF 85 USPATFULL on STN

TI Process of Preparing Esters and Ethers of Probucol and  
Derivatives  
Thereof

L11 ANSWER 16 OF 85 USPATFULL on STN  
TI Hardener for Epoxy Resin and Epoxy Resin Composition

L11 ANSWER 17 OF 85 USPATFULL on STN  
TI MICROBIAL TRANSFORMATION METHOD FOR THE PREPARATION OF AN  
EPOTHILONE

L11 ANSWER 18 OF 85 USPATFULL on STN  
TI \*\*\*MERCAPTAN\*\*\* -HARDENED EPOXY POLYMER COMPOSITIONS AND  
PROCESSES  
FOR MAKING AND USING SAME

L11 ANSWER 19 OF 85 USPATFULL on STN  
TI POLYMER COMPOSITIONS AND PROCESSES FOR MAKING AND USING SAME

L11 ANSWER 20 OF 85 USPATFULL on STN  
TI Copper-catalyzed formation of carbon-heteroatom and carbon-carbon  
bonds

L11 ANSWER 21 OF 85 USPATFULL on STN  
TI ORGANOMETALLIC COMPOSITIONS AND COATING COMPOSITIONS

L11 ANSWER 22 OF 85 USPATFULL on STN  
TI Pyrrolotriazine inhibitors of kinases

L11 ANSWER 23 OF 85 USPATFULL on STN  
TI Polythioethane compositions and processes for making and using  
same

L11 ANSWER 24 OF 85 USPATFULL on STN  
TI Retroviral protease inhibitors

L11 ANSWER 25 OF 85 USPATFULL on STN  
TI Retroviral protease inhibitors

L11 ANSWER 26 OF 85 USPATFULL on STN  
TI \*\*\*Thiol\*\*\* ester compositions and processes for making and  
using  
same

L11 ANSWER 27 OF 85 USPATFULL on STN  
TI Organometallic compositions and coating compositions

L11 ANSWER 28 OF 85 USPATFULL on STN  
TI Pyrrolotriazine inhibitors of kinases

L11 ANSWER 29 OF 85 USPATFULL on STN  
TI Controlled release fertilizer material and process for production  
thereof

L11 ANSWER 30 OF 85 USPATFULL on STN  
TI Pyrrolotriazine inhibitors of kinases

L11 ANSWER 31 OF 85 USPATFULL on STN  
TI Process of preparing esters and ethers of probucol and  
derivatives

thereof

L11 ANSWER 32 OF 85 USPATFULL on STN

TI Radiation-curable coatings for plastic substrates from  
multifunctional  
acrylate oligomers

L11 ANSWER 33 OF 85 USPATFULL on STN

TI Copper-catalyzed formation of carbon heteroatom and carbon-carbon  
bonds

L11 ANSWER 34 OF 85 USPATFULL on STN

TI Anionic and Lewis base photopolymerization process and its use  
for  
making optical articles

L11 ANSWER 35 OF 85 USPATFULL on STN

TI \*\*\*Thiol\*\*\* ester compositions and processes for making and  
using  
same

L11 ANSWER 36 OF 85 USPATFULL on STN

TI \*\*\*Thiol\*\*\* ester compositions and processes for making and  
using  
same

L11 ANSWER 37 OF 85 USPATFULL on STN

TI Compositions useful as coatings, their preparation, and articles  
made  
therefrom

L11 ANSWER 38 OF 85 USPATFULL on STN

TI Anionic and Lewis base photopolymerization process and its use  
for  
making optical articles

L11 ANSWER 39 OF 85 USPATFULL on STN

TI Photocrosslinked hydrogel blend surface coatings

L11 ANSWER 40 OF 85 USPATFULL on STN

TI Dual cure reaction products of self-photoinitiating  
multifunctional  
acrylates with \*\*\*thiols\*\*\* and synethetic methods

L11 ANSWER 41 OF 85 USPATFULL on STN

TI Photoactivable nitrogen bases

L11 ANSWER 42 OF 85 USPATFULL on STN

TI Novel mono- and di-fluorinated beozothiepine copmunds as  
inhibitors of  
apical sodium co-dependent bile acid transport (ASBT) and  
taurocholate  
uptake

L11 ANSWER 43 OF 85 USPATFULL on STN

TI Microbial transformation method for the preparation of an  
epothilone

L11 ANSWER 44 OF 85 USPATFULL on STN

TI Microbial transformation method for the preparation of an

epothilone

L11 ANSWER 45 OF 85 USPATFULL on STN

TI Derivatives of gambogic acid and analogs as activators of caspases and inducers of apoptosis

L11 ANSWER 46 OF 85 USPATFULL on STN

TI Method for anion-exchange adsorption and anion-exchangers

L11 ANSWER 47 OF 85 USPATFULL on STN

TI Novel mono- and di-fluorinated benzothiepine compounds as inhibitors of apical sodium co-dependent bile acid transport (ASBT) and taurocholate uptake

L11 ANSWER 48 OF 85 USPATFULL on STN

TI Dental polymer film

L11 ANSWER 49 OF 85 USPATFULL on STN

TI Copper-catalyzed formation of carbon-heteroatom and carbon-carbon bonds

L11 ANSWER 50 OF 85 USPATFULL on STN

TI Novel benzothiepinines having activity as inhibitors of ileal bile acid transport and taurocholate uptake

L11 ANSWER 51 OF 85 USPATFULL on STN

TI Lactacystin analogs

L11 ANSWER 52 OF 85 USPATFULL on STN

TI Process for the preparation of 3,7-disubstituted-2,3,4,5-tetrahydro-1H-1,4-benzodiazepine compounds

L11 ANSWER 53 OF 85 USPATFULL on STN

TI High strength epoxy adhesive and uses thereof

L11 ANSWER 54 OF 85 USPATFULL on STN

TI Copper-catalyzed formation of carbon-heteroatom and carbon-carbon bonds

L11 ANSWER 55 OF 85 USPATFULL on STN

TI Retroviral protease inhibitors

L11 ANSWER 56 OF 85 USPATFULL on STN

TI Composition of epoxy resin, chain extender and polymeric toughener with separate base catalyst

L11 ANSWER 57 OF 85 USPATFULL on STN

TI Inhibiting discoloration of halogen-containing polymers after radiation

L11 ANSWER 58 OF 85 USPATFULL on STN

TI Thiolamide curing agents

L11 ANSWER 59 OF 85 USPATFULL on STN

TI        Substituted 5-aryl-benzothiepies having activity as inhibitors  
of ileal  
          bile acid transport and taurocholate uptake

L11    ANSWER 60 OF 85    USPATFULL on STN  
TI        Primerless substrate repair with polyepoxide and polythiol

L11    ANSWER 61 OF 85    USPATFULL on STN  
TI        Reacting methylene and alkene components in presence of tertiary  
amine  
          reacted with    \*\*\*epoxide\*\*\*

L11    ANSWER 62 OF 85    USPATFULL on STN  
TI        Isocyanate reactive blends and internal mould release composites

L11    ANSWER 63 OF 85    USPATFULL on STN  
TI        Isocyanate reactive blends and internal mould release  
compositions

L11    ANSWER 64 OF 85    USPATFULL on STN  
TI        Heat-curable reaction resin mixtures and the use thereof

L11    ANSWER 65 OF 85    USPATFULL on STN  
TI        Thermally curable mixture containing epoxy and formamide  
compounds

L11    ANSWER 66 OF 85    USPATFULL on STN  
TI        Isocyanate reactive blends and internal mould release  
compositions

L11    ANSWER 67 OF 85    USPATFULL on STN  
TI        Decarboxylation processes using mixed metal oxide catalysts

L11    ANSWER 68 OF 85    USPATFULL on STN  
TI        Reaction product of olefinically unsaturated compounds with  
compounds  
          containing active hydrogen, processes for their preparation and  
2-component lacquers based thereon

L11    ANSWER 69 OF 85    USPATFULL on STN  
TI        Encapsulant compositions for use in signal transmission devices

L11    ANSWER 70 OF 85    USPATFULL on STN  
TI        Polyamines and a process for the production thereof

L11    ANSWER 71 OF 85    USPATFULL on STN  
TI        Reaction product of olefinically unsaturated compounds with  
compounds  
          containing active hydrogen, processes for their preparation and  
2-component lacquers based thereon HOE 85/F 036J

L11    ANSWER 72 OF 85    USPATFULL on STN  
TI        Tin or bismuth complex catalysts and trigger cure of coatings  
therewith

L11    ANSWER 73 OF 85    USPATFULL on STN  
TI        Rapid curing epoxy compositions

L11    ANSWER 74 OF 85    USPATFULL on STN  
TI        Epoxy/nucleophile transesterification catalysts and thermoset

coatings

L11 ANSWER 75 OF 85 USPATFULL on STN

TI Powder coatings with catalyzed transesterification cure

L11 ANSWER 76 OF 85 USPATFULL on STN

TI Heat-hardenable \*\*\*epoxide\*\*\* resin mixtures

L11 ANSWER 77 OF 85 USPATFULL on STN

TI Modified disulfide polymer composition and method for making same from

formal \*\*\*mercaptan\*\*\* terminated disulfide polymer and diethyl

\*\*\*mercaptan\*\*\* terminated polysulfide

L11 ANSWER 78 OF 85 USPATFULL on STN

TI Transesterification process

L11 ANSWER 79 OF 85 USPATFULL on STN

TI Polyamines and a process for their production

L11 ANSWER 80 OF 85 USPATFULL on STN

TI Process for the preparation of polyamines from N-monoaryl-N',N'-dialkyl

urea compounds and their use for the synthesis of polyurethanes

L11 ANSWER 81 OF 85 USPATFULL on STN

TI N-[2-Amino(oxy- or thia- group-substituted-cycloaliphatic)]benzeneacetamides and -benzamide analgesics

L11 ANSWER 82 OF 85 USPATFULL on STN

TI Process for the preparation of stabilized polymer dispersions in polyol

at low temperature

L11 ANSWER 83 OF 85 USPATFULL on STN

TI Broken-down organic lignin-cellulose silicate polymers

L11 ANSWER 84 OF 85 USPATFULL on STN

TI Polyepoxide curing by polymercaptans catalyzed by dimethylamino alkyl

ethers

L11 ANSWER 85 OF 85 USPATFULL on STN

TI High resilience flexible foamed polyurethanes, foamable mixtures and

process therefor

=> d 26,31,36 hit ibib

L11 ANSWER 26 OF 85 USPATFULL on STN

TI \*\*\*Thiol\*\*\* ester compositions and processes for making and using

same

AB \*\*\*Thiol\*\*\* ester compositions, methods of making the

\*\*\*thiol\*\*\*

ester compositions, and methods of using the \*\*\*thiol\*\*\*

ester

compositions are provided. In some embodiments, the \*\*\*thiol\*\*\*

ester compositions include \*\*\*thiol\*\*\* esters, hydroxy  
\*\*\*thiol\*\*\*  
esters and cross-linked \*\*\*thiol\*\*\* esters. The \*\*\*thiol\*\*\*  
ester composition can be used to produce cross-linked  
\*\*\*thiol\*\*\*  
esters, sulfonic acid-containing esters, sulfonate containing  
esters and  
thioacrylate containing esters. The \*\*\*thiol\*\*\* ester  
compositions  
can be used to produce polythiourethanes. The polythiourethanes  
can be  
used in fertilizers and fertilizer coatings.

SUMM The invention relates to \*\*\*thiol\*\*\* containing ester  
compositions  
generally made from a reaction of unsaturated ester compositions  
and a  
material capable of forming a \*\*\*thiol\*\*\* group. The  
invention also  
relates to the processes for preparing such \*\*\*thiol\*\*\*  
containing  
compositions and uses for the \*\*\*thiol\*\*\* containing  
compositions.

SUMM The present invention advantageously provides \*\*\*thiol\*\*\*  
containing compositions and methods of making such compositions.  
In  
addition to the compositions and methods of making such  
compositions,  
products that include such compositions are also provided.

SUMM As an embodiment of the present invention, a \*\*\*thiol\*\*\*  
ester  
composition is advantageously provided. In this embodiment, the  
\*\*\*thiol\*\*\* ester composition includes \*\*\*thiol\*\*\* ester  
molecules  
that have an average of at least 1.5 ester groups per  
\*\*\*thiol\*\*\*  
ester molecule. The \*\*\*thiol\*\*\* ester molecules also have an  
average  
of at least 1.5 \*\*\*thiol\*\*\* groups per \*\*\*thiol\*\*\* ester  
molecule. The \*\*\*thiol\*\*\* ester molecules also have a molar  
ratio of  
cyclic sulfides to \*\*\*thiol\*\*\* groups of less than 1.5.

SUMM In some aspects, the \*\*\*thiol\*\*\* ester molecules have a  
molar ratio  
of cyclic sulfides to \*\*\*thiol\*\*\* groups ranging from 0 to  
1.0. In  
some aspects, the \*\*\*thiol\*\*\* ester molecules have an average  
ranging from 1.5 to 9 \*\*\*thiol\*\*\* groups per \*\*\*thiol\*\*\*  
ester  
molecule. In some embodiments, the \*\*\*thiol\*\*\* ester  
molecules have  
a molar ratio of carbon-carbon double bonds to \*\*\*thiol\*\*\*  
groups of  
less than 1.5.

SUMM The amount of \*\*\*thiol\*\*\* sulfur or \*\*\*mercaptan\*\*\*  
sulfur  
contained within the \*\*\*thiol\*\*\* ester molecules can also

vary. For

example, in some embodiments, the \*\*\*thiol\*\*\* ester molecules have

an average of greater than 5 weight percent \*\*\*thiol\*\*\* sulfur. In

other embodiments, the \*\*\*thiol\*\*\* ester molecules have an average

ranging from 8 to 10 weight percent \*\*\*thiol\*\*\* sulfur. In some

embodiments, the \*\*\*thiol\*\*\* ester molecules have an average of less

than 30 mole percent sulfur, which is present as cyclic sulfides. Alternatively, the \*\*\*thiol\*\*\* ester molecules have an

average of less than 2 mole percent sulfur present as cyclic sulfides.

SUMM In some embodiments, the \*\*\*thiol\*\*\* ester molecules are produced

from unsaturated esters that have an average of less than 25 weight

percent of side chains that include 3 contiguous methylene interrupted

carbon-carbon double bonds. In another aspect, greater than 40 percent

of the total side chains contained within the \*\*\*thiol\*\*\* ester

molecules contain sulfur.

SUMM In addition to the \*\*\*thiol\*\*\* ester composition, a process for

producing the \*\*\*thiol\*\*\* ester composition is advantageously provided as another embodiment of the present invention. To

produce the \*\*\*thiol\*\*\* ester composition, hydrogen sulfide is contacted

with an unsaturated ester composition. The unsaturated ester composition

includes unsaturated esters that have an average of at least 1.5

ester groups per unsaturated ester molecule. The unsaturated esters also have

an average of at least 1.5 carbon-carbon double bonds per unsaturated

ester molecule. The hydrogen sulfide and the unsaturated esters are

reacted to produce or form the \*\*\*thiol\*\*\* ester composition. The

\*\*\*thiol\*\*\* ester composition advantageously includes \*\*\*thiol\*\*\*

ester molecules that have a molar ratio of cyclic sulfides to \*\*\*thiol\*\*\*

groups of less than 1.5.

SUMM Another process for producing the \*\*\*thiol\*\*\* ester composition is

advantageously provided as another embodiment of the present invention.

In this process embodiment, the hydrogen sulfide and the unsaturated

ester composition are contacted. The unsaturated ester composition

includes unsaturated esters having an average of at least 1.5



ester groups per unsaturated ester molecule and having an average of at least 1.5 carbon-carbon double bonds per unsaturated ester molecule. The hydrogen sulfide and the unsaturated esters are then reacted in a substantial absence of a solvent to form the \*\*\*thiol\*\*\* ester composition. The \*\*\*thiol\*\*\* ester composition includes \*\*\*thiol\*\*\* ester molecules. The \*\*\*thiol\*\*\* ester composition advantageously includes \*\*\*thiol\*\*\* ester molecules that have a molar ratio of cyclic sulfides to \*\*\*thiol\*\*\* groups of less than 1.5.

SUMM The resulting \*\*\*thiol\*\*\* ester molecules produced by this process possess advantageous characteristics. For example, in some embodiments, the \*\*\*thiol\*\*\* ester molecules have a molar ratio of the hydrogen sulfide to carbon-carbon double bonds of greater than 2. As another example, in other embodiments, the \*\*\*thiol\*\*\* ester molecules have an average of greater than 5 weight percent \*\*\*thiol\*\*\* sulfur. In some aspects, greater than 40 percent of the \*\*\*thiol\*\*\* ester molecule total side chains contain sulfur.

SUMM As another embodiment of the present invention, another process for preparing the \*\*\*thiol\*\*\* ester composition is advantageously provided. In this embodiment, a polyol composition and a \*\*\*thiol\*\*\* carboxylic acid composition are contacted and reacted to produce the \*\*\*thiol\*\*\* ester composition. The \*\*\*thiol\*\*\* ester composition includes \*\*\*thiol\*\*\* ester molecules having an average of at least 1.5 ester groups per \*\*\*thiol\*\*\* ester molecule and having an average of at least 1.5 \*\*\*thiol\*\*\* groups per \*\*\*thiol\*\*\* ester molecule.

SUMM In addition to the \*\*\*thiol\*\*\* ester composition, other compositions are advantageously provided as embodiments of the present invention. For example, a hydroxy \*\*\*thiol\*\*\* ester composition is provided as another embodiment of the present invention. The hydroxyl \*\*\*thiol\*\*\* ester composition includes hydroxy \*\*\*thiol\*\*\* ester molecules having an average of at least 1.5 ester groups per hydroxy

1.5           \*\*\*thiol\*\*\* ester molecule and having an average of at least  
          .alpha.-hydroxy   \*\*\*thiol\*\*\* groups per hydroxy   \*\*\*thiol\*\*\*  
ester molecule.

SUMM   As described herein, the .alpha.-hydroxy   \*\*\*thiol\*\*\* groups  
contain  
          an alcohol or hydroxy group and a   \*\*\*thiol\*\*\* group within  
the same  
          group. In embodiments of the present invention, the .alpha.-  
hydroxy

          \*\*\*thiol\*\*\* groups can be replaced with separate alcohol and  
          \*\*\*thiol\*\*\* groups. In these embodiments, the same number of  
.alpha.-hydroxy groups can be used for the separate alcohol and  
          \*\*\*thiol\*\*\* groups. For example, in some embodiments, the  
hydroxy

          \*\*\*thiol\*\*\* ester molecules have an average of at least 1.5  
.alpha.-hydroxy   \*\*\*thiol\*\*\* groups. In embodiments that  
contain  
          separate alcohol and   \*\*\*thiol\*\*\* groups, the hydroxy  
\*\*\*thiol\*\*\*  
          ester molecules would contain an average of at least 1.5 alcohol  
groups  
          and an average of at least 1.5   \*\*\*thiol\*\*\* groups.

SUMM   In some aspects, the hydroxy   \*\*\*thiol\*\*\* ester molecules  
have an  
          average ranging from 1.5 to 9 .alpha.-hydroxy   \*\*\*thiol\*\*\*  
groups per  
          hydroxy   \*\*\*thiol\*\*\* ester molecule. In some embodiments, the  
          \*\*\*thiol\*\*\* ester molecules have a molar ratio of carbon-  
carbon double  
          bonds to   \*\*\*thiol\*\*\* groups of less than 1.5.

SUMM   In some embodiments, the   \*\*\*thiol\*\*\* ester molecules are  
produced  
          from unsaturated esters that have an average of less than 25  
weight  
          percent of side chains that include 3 contiguous methylene  
interrupted  
          carbon-carbon double bonds. In another aspect, greater than 40  
percent  
          of the total side chains contained within the .alpha.-hydroxy  
          \*\*\*thiol\*\*\* ester molecules contain sulfur.

SUMM   The amount of   \*\*\*thiol\*\*\* sulfur contained within the  
hydroxy  
          \*\*\*thiol\*\*\* ester molecules can also vary. For example, in  
some  
          embodiments, the hydroxy   \*\*\*thiol\*\*\* ester molecules have an  
average  
          of greater than 5 weight percent   \*\*\*thiol\*\*\* sulfur. In other  
embodiments, the hydroxy   \*\*\*thiol\*\*\* ester molecules have an  
average  
          ranging from 8 to 10 weight percent   \*\*\*thiol\*\*\* sulfur.

SUMM   In some embodiments, the hydroxy   \*\*\*thiol\*\*\* ester molecules  
have a  
          molar ratio of   \*\*\*epoxide\*\*\* groups to the .alpha.-hydroxy

\*\*\*thiol\*\*\* groups of less than 2. In other aspects, the composition is substantially free of \*\*\*epoxide\*\*\* groups.

SUMM In addition to the hydroxy \*\*\*thiol\*\*\* ester composition, methods or processes for making the hydroxy \*\*\*thiol\*\*\* ester composition are advantageously provided as embodiments of the present invention. In an embodiment, a process for preparing the hydroxy \*\*\*thiol\*\*\* ester composition is provided that includes the step of contacting the hydrogen sulfide and an epoxidized unsaturated ester composition. The epoxidized unsaturated ester composition includes epoxidized unsaturated esters having an average of at least 1.5 ester groups per epoxidized unsaturated ester molecule and having an average of at least 1.5 \*\*\*epoxide\*\*\* groups per epoxidized unsaturated ester molecule. The hydrogen sulfide and the epoxidized unsaturated esters are then reacted to form the hydroxy \*\*\*thiol\*\*\* ester composition.

SUMM In some embodiments, a molar ratio of the hydrogen sulfide to \*\*\*epoxide\*\*\* groups in the epoxidized unsaturated esters is greater than 1.

SUMM Another process for preparing the hydroxy \*\*\*thiol\*\*\* ester composition is advantageously provided as another embodiment of the present invention. In this process embodiment, a polyol composition and a hydroxy \*\*\*thiol\*\*\* carboxylic acid composition are contacted and reacted to produce the hydroxy \*\*\*thiol\*\*\* ester composition. In this embodiment, the hydroxy \*\*\*thiol\*\*\* ester composition includes hydroxy \*\*\*thiol\*\*\* ester molecules having an average of at least 1.5 ester groups per hydroxy \*\*\*thiol\*\*\* ester molecule and having an average of at least 1.5 .alpha.-hydroxy \*\*\*thiol\*\*\* groups per hydroxy \*\*\*thiol\*\*\* ester molecule.

SUMM A cross-linked \*\*\*thiol\*\*\* ester composition is advantageously provided as another embodiment of the present invention. The cross-linked \*\*\*thiol\*\*\* ester composition includes \*\*\*thiol\*\*\* ester oligomers having at least two \*\*\*thiol\*\*\* ester monomers connected by a polysulfide linkage having a structure --S.sub.Q--, wherein Q is greater than 1. In some embodiments, the

\*\*\*thiol\*\*\*

ester oligomers have at least three \*\*\*thiol\*\*\* ester monomers

connected by polysulfide linkages. In another aspect, the

\*\*\*thiol\*\*\*

ester oligomers have from 3 to 20 \*\*\*thiol\*\*\* ester monomers connected by polysulfide linkages.

SUMM In an aspect, the cross-linked \*\*\*thiol\*\*\* ester composition includes both \*\*\*thiol\*\*\* ester monomers and \*\*\*thiol\*\*\* ester

oligomers. In some embodiments, the \*\*\*thiol\*\*\* ester monomers and

\*\*\*thiol\*\*\* ester oligomers have a total \*\*\*thiol\*\*\* sulfur

content ranging from 0.5 to 8 weight percent; or alternatively, ranging

from 8 to 15 weight percent. The combined \*\*\*thiol\*\*\* ester monomers

and \*\*\*thiol\*\*\* ester oligomers can have an average molecular weight

greater than 2000; or alternatively, in a range from 2000 to 20,000.

SUMM As another embodiment of the present invention, a cross-linked \*\*\*thiol\*\*\* ester composition produced by the process comprising the

steps of contacting the \*\*\*thiol\*\*\* ester composition with an oxidizing agent and reacting the \*\*\*thiol\*\*\* ester and the oxidizing

agent to form \*\*\*thiol\*\*\* ester oligomers is advantageously provided. In this embodiment, the \*\*\*thiol\*\*\* ester oligomers have

at least two \*\*\*thiol\*\*\* ester monomers connected by a polysulfide

linkage having a structure --S.sub.Q--, wherein Q is greater than 1.

SUMM A process to produce the cross-linked \*\*\*thiol\*\*\* ester composition

is also advantageously provided as another embodiment of the present

invention. In this process, a \*\*\*thiol\*\*\* ester composition is

contacted and reacted with an oxidizing agent to form \*\*\*thiol\*\*\*

ester oligomers having at least two \*\*\*thiol\*\*\* ester monomers

connected by a polysulfide linkage having a structure --S.sub.Q--,

wherein Q is greater than 1. In some embodiments, the oxidizing agent is

elemental sulfur, oxygen, or hydrogen peroxide. In an aspect, the oxidizing agent is elemental sulfur.

SUMM In an aspect, the \*\*\*thiol\*\*\* ester is a hydroxy \*\*\*thiol\*\*\*

ester. In other aspects, a weight ratio of elemental sulfur to \*\*\*thiol\*\*\* sulfur in the \*\*\*thiol\*\*\* ester molecules

ranges from

0.5 to 32.

SUMM The step of the reacting the \*\*\*thiol\*\*\* ester and the oxidizing agent can be performed at a temperature ranging from 25.degree. C. to 150.degree. C. The process for producing the cross-linked \*\*\*thiol\*\*\* ester composition can also include the step of stripping residual hydrogen sulfide from the cross-linked \*\*\*thiol\*\*\* ester composition produced. In another aspect, the reaction of the \*\*\*thiol\*\*\* ester and the elemental sulfur is catalyzed. In some embodiments, the catalyst is an amine.

SUMM In another of its aspects, the present invention relates to a controlled release fertilizer material comprising a particulate plant nutrient surrounded by a coating which is the reaction product of a mixture comprising: (i) a first component selected from an isocyanate and/or an epoxy resin, and (ii) a first active hydrogen-containing compound selected from the group consisting of: a \*\*\*thiol\*\*\* ester composition; a hydroxy \*\*\*thiol\*\*\* ester composition; a cross-linked \*\*\*thiol\*\*\* ester composition and mixtures thereof.

SUMM In another of its aspects, the present invention relates to a process for the production of abrasion resistant polythiourethane and/or epoxy polymer encapsulated controlled release fertilizer particles by incorporating in urethane and/or epoxy polymer forming reaction mixture a sulfur-containing compound such as one or more of a \*\*\*thiol\*\*\* ester composition; a hydroxy \*\*\*thiol\*\*\* ester composition; a cross-linked \*\*\*thiol\*\*\* ester composition, other sulfur-based compounds described herein below and mixtures thereof.

SUMM Preferably, for the production of the present polythiourethane encapsulated controlled release fertilizer material, a sulfur-containing compound (e.g., one or more of a \*\*\*thiol\*\*\* ester composition; a hydroxy \*\*\*thiol\*\*\* ester composition; a cross-linked \*\*\*thiol\*\*\* ester composition) is used as one of the isocyanate-reactive components (alone or in combination with other active hydrogen-containing compounds). Preferably, the sulfur-containing compound comprises a sulfur-containing vegetable oil. In one preferred embodiment, the sulfur-containing vegetable oil comprises a mercaptanized

vegetable oil  
(MVO), more preferably as described in more detail herein, even  
more preferably an MVO produced by the addition of hydrogen sulfide to  
a vegetable oil. In another preferred embodiment, the sulfur-  
containing vegetable oil comprises mercapto-hydroxy vegetable oil (MHVO),  
more preferably as described in more detail herein, even more  
preferably an MHVO produced by the addition of hydrogen sulfide to epoxidized  
vegetable oil. In yet another preferred embodiment, the sulfur  
containing vegetable oil comprises sulfur cross-linked  
mercaptanized vegetable oil (CMVO), more preferably as described in more detail  
herein, even more preferably an CMVO produced by the addition of  
elemental sulfur to mercaptanized vegetable oil (MVO).

SUMM Preferably, for the production of epoxy polymer encapsulated  
controlled release fertilizer material, a sulfur-containing compound (e.g.,  
one or more of a \*\*\*thiol\*\*\* ester composition; a hydroxy  
\*\*\*thiol\*\*\* ester composition; a cross-linked \*\*\*thiol\*\*\* ester  
composition) is used as one of the isocyanate-reactive components (alone or in  
combination with other active hydrogen-containing compounds).  
Preferably, the sulfur-containing compound comprises a sulfur-  
containing vegetable oil (e.g., MVO and/or MHVO and/or CMVO) is used as one  
of the epoxy resin-reactive components.

DRWD FIG. 1 includes two graphs that compare the NMR's of soybean  
oil, which is shown in the top graph, and a \*\*\*thiol\*\*\* containing ester  
produced from soybean oil in accordance with an embodiment of the  
present invention, which is shown in the bottom graph;

DRWD FIG. 2 includes two graphs that compare the NMR's of epoxidized  
soybean oil, which is shown in the top graph, and a \*\*\*thiol\*\*\*  
containing ester produced from epoxidized soybean oil in accordance with an  
embodiment of the present invention, which is shown in the bottom  
graph;

DRWD FIG. 3 is a gas chromatograph (GC)/mass spectrometer (MS) trace  
of a

\*\*\*thiol\*\*\* containing ester that was produced from soybean  
oil in accordance with an embodiment of the present invention and then  
treated by methanolysis;

DRWD FIG. 5 is a GC/MS trace of hydroxy \*\*\*thiol\*\*\* containing  
ester produced from epoxidized soybean oil in accordance with an  
embodiment of

the present invention and then treated by methanolysis;  
DETD In this specification, " \*\*\*thiol\*\*\* ester composition"

refers to an ester composition that includes " \*\*\*thiol\*\*\* ester molecules." The \*\*\*thiol\*\*\* ester molecule has at least one \*\*\*thiol\*\*\* group and at least one ester group within the \*\*\*thiol\*\*\* ester molecule.

DETD In this specification, "hydroxy \*\*\*thiol\*\*\* ester composition" refers to an ester composition that includes "hydroxy \*\*\*thiol\*\*\* ester molecules." The hydroxy \*\*\*thiol\*\*\* ester molecule has at least one \*\*\*thiol\*\*\* group, at least one ester group, and at least one hydroxy or alcohol group within the hydroxy \*\*\*thiol\*\*\* ester molecule. Alternatively, the alcohol group and the \*\*\*thiol\*\*\* group can be combined in the same group, which is referred to as an ".alpha.-hydroxy \*\*\*thiol\*\*\* group."

DETD In this specification, "polythiourethane" refers to a urethane composition that includes more than one of the following structure:

##STR1## The presence of the thiourethane group can be determined by method known to those skilled in the art (for example infrared spectroscopy, Raman spectroscopy, and/or NMR). \*\*\*Thiol\*\*\*

Ester Composition

DETD The present invention advantageously provides a \*\*\*thiol\*\*\* ester composition as an embodiment of the present invention. The \*\*\*thiol\*\*\* ester composition includes \*\*\*thiol\*\*\* ester molecules that have an average of at least 1.5 ester groups and an average of at least 1.5 \*\*\*thiol\*\*\* groups per \*\*\*thiol\*\*\* ester molecule. The \*\*\*thiol\*\*\* ester composition also has a molar ratio of cyclic sulfides to \*\*\*thiol\*\*\* groups of less than 1.5, as described herein.

DETD Generally, the \*\*\*thiol\*\*\* ester composition contains molecules having at least one ester group and at least one \*\*\*thiol\*\*\* group. The \*\*\*thiol\*\*\* ester composition of this invention can be produced from any unsaturated ester, as described herein. Because the feedstock unsaturated esters can contain multiple carbon-carbon double bonds per unsaturated ester molecule, carbon-carbon double bond reactivity and statistical probability dictate that each \*\*\*thiol\*\*\* ester molecule of the \*\*\*thiol\*\*\* ester composition produced from the unsaturated ester composition will not have the same number of \*\*\*thiol\*\*\*

groups, number of unreacted carbon-carbon double bonds, number of  
 cyclic  
 sulfides, molar ratio of carbon-carbon double bonds to  
 \*\*\*thiol\*\*\*  
 groups, molar ratio of cyclic sulfides to \*\*\*thiol\*\*\* groups  
 and  
 other quantities of functional groups and molar ratios disclosed  
 herein  
 as the feedstock unsaturated ester. Additionally, the feedstock  
 unsaturated esters can also comprise a mixture of individual  
 unsaturated  
 esters having a different number of carbon-carbon double bonds  
 and/or  
 ester groups. Thus, many of these properties will be discussed as  
 an  
 average number of the groups per \*\*\*thiol\*\*\* ester molecule  
 within  
 the \*\*\*thiol\*\*\* ester composition or average ratio per  
 \*\*\*thiol\*\*\*  
 ester molecule within the \*\*\*thiol\*\*\* ester composition. In  
 other  
 embodiments, it is desired to control the content of  
 \*\*\*thiol\*\*\*  
 sulfur present in the \*\*\*thiol\*\*\* ester. Because it is  
 difficult to  
 ensure that the hydrogen sulfide reacts with every carbon-carbon  
 double  
 bond within the unsaturated ester, certain molecules of  
 \*\*\*thiol\*\*\*  
 ester can have more or less \*\*\*thiol\*\*\* groups than other  
 molecules.  
 Thus, the weight percent of \*\*\*thiol\*\*\* groups is stated as  
 an  
 average across all \*\*\*thiol\*\*\* ester molecules of the  
 \*\*\*thiol\*\*\*  
 ester composition.  
 DETD The \*\*\*thiol\*\*\* ester can be derived from any unsaturated  
 ester  
 described herein.  
 DETD The \*\*\*thiol\*\*\* ester compositions can be described as  
 comprising  
 one or more separate or discreet functional groups of the  
 \*\*\*thiol\*\*\*  
 ester molecule and/or \*\*\*thiol\*\*\* ester composition. These  
 independent functional groups can include: the number of (or  
 average  
 number of) ester groups per \*\*\*thiol\*\*\* ester molecule,  
 \*\*\*thiol\*\*\* containing the number of (or average number of)  
 \*\*\*thiol\*\*\* groups per \*\*\*thiol\*\*\* ester molecule, the  
 number of  
 (or average number of) unreacted carbon-carbon double bonds per  
 \*\*\*thiol\*\*\* ester molecule, the average \*\*\*thiol\*\*\*  
 sulfur content  
 of the \*\*\*thiol\*\*\* ester composition, the percentage (or  
 average  
 percentage) of sulfide linkages per \*\*\*thiol\*\*\* ester  
 molecule, and  
 the percentage (or average percentage) of cyclic sulfide groups  
 per  
 \*\*\*thiol\*\*\* ester molecule. Additionally, the \*\*\*thiol\*\*\*



ester compositions can be described using individual or a combination of ratios including the ratio of double bonds to \*\*\*thiol\*\*\* groups, the ratio of cyclic sulfides to \*\*\*mercaptan\*\*\* group, and the like. As separate elements, these functional groups of the \*\*\*thiol\*\*\* composition will be described separately.

DETD Minimally, in some embodiments, the \*\*\*thiol\*\*\* ester contains \*\*\*thiol\*\*\* ester molecules having at least one ester group and one \*\*\*thiol\*\*\* group per \*\*\*thiol\*\*\* ester molecule. As the \*\*\*thiol\*\*\* ester is prepared from unsaturated esters, the \*\*\*thiol\*\*\* ester can contain the same number of ester groups as the unsaturated esters described herein. In an embodiment, the \*\*\*thiol\*\*\* ester molecules have an average of at least 1.5 ester groups per \*\*\*thiol\*\*\* ester molecule. Alternatively, the \*\*\*thiol\*\*\* ester molecules have an average of at least 2 ester groups per \*\*\*thiol\*\*\* ester molecule; alternatively, an average of at least 2.5 ester groups per \*\*\*thiol\*\*\* ester molecule; or alternatively, an average of at least 3 ester groups per \*\*\*thiol\*\*\* ester molecule. In other embodiments, the \*\*\*thiol\*\*\* esters have an average of from 1.5 to 8 ester groups per \*\*\*thiol\*\*\* ester molecule; alternatively, an average of from 2 to 7 ester groups per \*\*\*thiol\*\*\* ester molecule; alternatively, an average of from 2.5 to 5 ester groups per \*\*\*thiol\*\*\* ester molecule; or alternatively, an average of from 3 to 4 ester groups per \*\*\*thiol\*\*\* ester molecule. In yet other embodiments, the \*\*\*thiol\*\*\* ester comprises an average of 3 ester groups per \*\*\*thiol\*\*\* ester molecule or alternatively, an average of 4 ester groups per unsaturated ester molecule.

DETD Minimally, the \*\*\*thiol\*\*\* ester comprises an average of at least one \*\*\*thiol\*\*\* group per \*\*\*thiol\*\*\* ester molecule. In an embodiment, the \*\*\*thiol\*\*\* ester molecules have an average of at least 1.5 \*\*\*thiol\*\*\* groups per \*\*\*thiol\*\*\* ester molecule; alternatively, \*\*\*thiol\*\*\* containing an average of at least 2 \*\*\*thiol\*\*\* groups per \*\*\*thiol\*\*\* ester molecule; alternatively, an average of at least 2.5 \*\*\*thiol\*\*\* groups per \*\*\*thiol\*\*\* ester molecule; or alternatively, an average of at least 3

\*\*\*thiol\*\*\*  
 groups per \*\*\*thiol\*\*\* ester molecule. In other embodiments,  
 the  
 \*\*\*thiol\*\*\* ester molecules have an average of from 1.5 to 9  
 \*\*\*thiol\*\*\* groups per \*\*\*thiol\*\*\* ester molecule;  
 alternatively,  
 an average of from 3 to 8 \*\*\*thiol\*\*\* groups per  
 \*\*\*thiol\*\*\*  
 ester molecule; alternatively, \*\*\*thiol\*\*\* containing an  
 average of  
 from 2 to 4 \*\*\*thiol\*\*\* groups per \*\*\*thiol\*\*\* ester  
 molecule,  
 or alternatively, an average of from 4 to 8 \*\*\*thiol\*\*\*  
 groups per  
 \*\*\*thiol\*\*\* ester molecule.

DETD In other embodiments, the \*\*\*thiol\*\*\* ester can be described  
 by the  
 average amount of \*\*\*thiol\*\*\* sulfur present in \*\*\*thiol\*\*\*  
 ester. In an embodiment, the \*\*\*thiol\*\*\* ester molecules have  
 an  
 average of at least 5 weight percent \*\*\*thiol\*\*\* sulfur per  
 \*\*\*thiol\*\*\* ester molecule; alternatively, an average of at  
 least 10  
 weight percent \*\*\*thiol\*\*\* sulfur per \*\*\*thiol\*\*\* ester  
 molecule, or alternatively, an average of greater than 15 weight  
 percent  
 \*\*\*thiol\*\*\* sulfur per \*\*\*thiol\*\*\* ester molecule. In an  
 embodiment, the \*\*\*thiol\*\*\* ester molecules have an average  
 of from  
 5 to 25 weight percent \*\*\*thiol\*\*\* sulfur per \*\*\*thiol\*\*\*  
 ester  
 molecule; alternatively, an average of from 5 to 20 weight  
 percent  
 \*\*\*thiol\*\*\* sulfur per \*\*\*thiol\*\*\* ester molecule;  
 alternatively,  
 an average of from 6 to 15 weight percent \*\*\*thiol\*\*\* sulfur  
 per  
 \*\*\*thiol\*\*\* ester molecule; or alternatively, an average of  
 from 8 to  
 10 weight percent \*\*\*thiol\*\*\* sulfur per \*\*\*thiol\*\*\*  
 ester  
 molecule.

DETD Generally, the location of the \*\*\*thiol\*\*\* group of the  
 \*\*\*thiol\*\*\* ester is not particularly important and will be  
 dictated  
 by the method used to produce the \*\*\*thiol\*\*\* ester. In  
 embodiments  
 wherein the \*\*\*thiol\*\*\* ester is produced by contacting an  
 unsaturated ester, the position of the \*\*\*thiol\*\*\* group will  
 be  
 dictated by the position of the carbon-carbon double bond. When  
 the  
 carbon-carbon double bond is an internal carbon-carbon double  
 bond, the  
 method of producing the \*\*\*thiol\*\*\* ester will result in a  
 secondary  
 \*\*\*thiol\*\*\* group. However, when the double bond is located  
 at a  
 terminal position it is possible to choose reaction conditions to  
 produce a \*\*\*thiol\*\*\* ester comprising either a primary

\*\*\*thiol\*\*\* group or a secondary \*\*\*thiol\*\*\* group.  
 DETD Some methods of producing the \*\*\*thiol\*\*\* ester composition  
 can additionally create sulfur containing functional groups other  
 than a \*\*\*thiol\*\*\* group. For example, in some \*\*\*thiol\*\*\* ester  
 production methods, an introduced \*\*\*thiol\*\*\* group can react  
 with a carbon-carbon double bond within the same unsaturated ester to  
 produce a sulfide linkage. When the reaction is with a double bond of a  
 second unsaturated ester, this produces a simple sulfide linkage.  
 However, in some instances, the second carbon-carbon double bond is located  
 in the same unsaturated ester molecule. When the \*\*\*thiol\*\*\* group  
 reacts with a second carbon-carbon double bond within the same  
 unsaturated ester molecule, a sulfide linkage is produced. In some instances,  
 the carbon-carbon double bond can be within a second ester group of  
 the unsaturated ester molecule. While in other instances, the carbon-  
 carbon double bond can be within the same ester group of the unsaturated  
 ester molecule.  
 DETD When the \*\*\*thiol\*\*\* group reacts with the carbon-carbon  
 double bond in a second ester group of the same unsaturated ester  
 molecule, the cyclic sulfide would contain two ester groups contained within a  
 ring structure. When the \*\*\*thiol\*\*\* group reacts with the carbon-  
 carbon double bond within the same ester group, the cyclic sulfide would  
 not contain an ester group within the ring structure. Within this  
 specification, this second type of cyclic sulfide is referred to  
 as a cyclic sulfide. Within this specification, the first type of  
 cyclic sulfide is referred to as a simple sulfide. In the cyclic sulfide  
 case, the sulfide linkage produces a cyclic sulfide functionality  
 within a single ester group of the \*\*\*thiol\*\*\* ester. This linkage is  
 termed a cyclic sulfide for purposes of this application. One such  
 sulfide group that can be produced is a cyclic sulfide. The cyclic  
 sulfide rings that can be produced include a tetrahydrothiopyran ring, a  
 thietane ring, or a thiophane ring (tetrahydrothiophene ring).  
 DETD In some embodiments, it is desirable to control the average  
 amount of sulfur present as cyclic sulfide in the \*\*\*thiol\*\*\* ester. In

an embodiment the average amount of sulfur present as cyclic sulfide in the \*\*\*thiol\*\*\* ester molecules comprises less than 30 mole percent. Alternatively, the average amount of sulfur present as cyclic sulfide in the \*\*\*thiol\*\*\* esters comprises less than 20 mole percent; alternatively, less than 10 mole percent; alternatively, less than 5 mole percent; or alternatively, less than 2 mole percent. In other embodiments, it is desired to control the molar ratio of cyclic sulfides to \*\*\*thiol\*\*\* groups. In other embodiments, it is desirable to have molar ratios of cyclic sulfide to \*\*\*thiol\*\*\* group. In an embodiment, the average molar ratio of cyclic sulfide groups to \*\*\*thiol\*\*\* group per \*\*\*thiol\*\*\* ester is less than 1.5. Alternatively, the average molar ratio of cyclic sulfide groups to \*\*\*thiol\*\*\* group per \*\*\*thiol\*\*\* ester is less than 1; alternatively, less than 0.5; alternatively, less than 0.25; or alternatively, 0.1. In some embodiments, the ratio of cyclic sulfide groups to \*\*\*thiol\*\*\* group per \*\*\*thiol\*\*\* ester ranges from 0 to 1; or alternatively, the average molar ratio of cyclic sulfide groups to \*\*\*thiol\*\*\* group per \*\*\*thiol\*\*\* ester ranges between 0.05 and 1.

DETD In some instances it can be desirable to have carbon-carbon double bonds present in the \*\*\*thiol\*\*\* ester composition while in other embodiments it can be desirable to minimize the number of carbon-carbon double bonds present in the \*\*\*thiol\*\*\* ester composition.

The presence of carbon-carbon double bonds present in the \*\*\*thiol\*\*\* ester can be stated as an average molar ratio of carbon-carbon double bonds to \*\*\*thiol\*\*\* -sulfur. In an embodiment, the average ratio of the remaining unreacted carbon-carbon double bond in the \*\*\*thiol\*\*\* ester composition to \*\*\*thiol\*\*\* sulfur is less than 1.5 per \*\*\*thiol\*\*\* ester molecule. Alternatively, the average ratio of carbon-carbon double bond to \*\*\*thiol\*\*\* sulfur is less than 1.2 per \*\*\*thiol\*\*\* ester molecule; alternatively, less than 1.0 per \*\*\*thiol\*\*\* ester molecule; alternatively, less than 0.75 per \*\*\*thiol\*\*\* ester molecule; alternatively, less than 0.5 per \*\*\*thiol\*\*\* ester molecule; alternatively, less than 0.2 per \*\*\*thiol\*\*\* ester molecule; or alternatively, less than 0.1 per \*\*\*thiol\*\*\* ester molecule.

DETD In particular embodiments, the \*\*\*thiol\*\*\* ester is produced

from unsaturated ester compositions. Because the feedstock unsaturated ester has particular compositions having a certain number of ester groups present, the product \*\*\*thiol\*\*\* ester composition will have about the same number of ester groups per \*\*\*thiol\*\*\* ester molecule as the feedstock unsaturated ester. Other, independent \*\*\*thiol\*\*\* ester properties described herein can be used to further describe the

\*\*\*thiol\*\*\* ester composition.  
DETD In some embodiments, the \*\*\*thiol\*\*\* ester molecules are produced from unsaturated esters having an average of less than 25 weight percent of side chains having 3 contiguous methylene interrupted carbon-carbon double bonds, as described herein. In some embodiments, greater than 40 percent of the \*\*\*thiol\*\*\* containing natural source total side chains can include sulfur. In some embodiments, greater than 60 percent of the \*\*\*thiol\*\*\* ester molecule total side chains can include sulfur. In other embodiments, greater than 50, 70, or 80 percent of the \*\*\*thiol\*\*\* ester molecule total side chains can include sulfur.

DETD In an embodiment, the \*\*\*thiol\*\*\* ester is a \*\*\*thiol\*\*\* containing natural source oil, as described herein. When the \*\*\*thiol\*\*\* ester is a \*\*\*thiol\*\*\* containing natural source oil, functional groups that are present in the \*\*\*thiol\*\*\* containing natural source oil can be described in a "per \*\*\*thiol\*\*\* ester molecule" basis or in a "per triglyceride" basis. The \*\*\*thiol\*\*\*

containing natural source oil can have substantially the same properties as the \*\*\*thiol\*\*\* ester composition, such as the molar ratios and other independent descriptive elements described herein.

DETD The average number of \*\*\*thiol\*\*\* groups per triglyceride in the \*\*\*thiol\*\*\* containing natural source oil is greater than about 1.5.

In some embodiments, the average number of \*\*\*thiol\*\*\* groups per triglyceride can range from about 1.5 to about 9.

DETD The \*\*\*thiol\*\*\* ester compositions can also be described as a product produced by the process comprising contacting hydrogen sulfide and an unsaturated ester composition and can be further limited by the process as described herein. The \*\*\*thiol\*\*\* containing

natural source oil can also be described using a molecular weight or an average molecular weight of the side chains.

DETD Hydroxy \*\*\*Thiol\*\*\* Ester Composition

DETD In embodiments of the present invention, the \*\*\*thiol\*\*\* ester compositions can also contain a hydroxy or alcohol group. When the \*\*\*thiol\*\*\* ester composition includes the hydroxy group, the \*\*\*thiol\*\*\* ester composition is referred to herein as the hydroxy \*\*\*thiol\*\*\* ester composition. The quantity or number of alcohol groups present in the hydroxy \*\*\*thiol\*\*\* ester composition can be independent of the quantity of other functional groups present in the hydroxy \*\*\*thiol\*\*\* ester composition (i.e. \*\*\*thiol\*\*\* ester groups, sulfides, cyclic sulfides). Additionally, the weight percent of \*\*\*thiol\*\*\* sulfur and functional group ratios (i.e. molar ratio of cyclic sulfides to \*\*\*thiol\*\*\* groups, molar ratio of \*\*\*epoxide\*\*\* groups to \*\*\*thiol\*\*\* groups, molar ratio of \*\*\*epoxide\*\*\* groups to .alpha.-hydroxy \*\*\*thiol\*\*\* groups and other disclosed quantities of functional groups and their molar ratios to the \*\*\*thiol\*\*\* groups) are separate or discreet elements that can be used to describe the hydroxy \*\*\*thiol\*\*\* ester composition.

The hydroxy \*\*\*thiol\*\*\* ester composition can be described using any combination of the hydroxy \*\*\*thiol\*\*\* ester composition separate functional groups or ratios described herein.

DETD In an embodiment, the hydroxy \*\*\*thiol\*\*\* ester composition is produced by reacting hydrogen sulfide with an epoxidized unsaturated ester composition as described herein. Because the epoxidized unsaturated ester can contain multiple \*\*\*epoxide\*\*\* groups, \*\*\*epoxide\*\*\* group reactivity and statistical probability dictate that not all hydroxy \*\*\*thiol\*\*\* ester molecules of the hydroxy \*\*\*thiol\*\*\* ester composition will have the same number of hydroxy groups, \*\*\*thiol\*\*\* groups, .alpha.-hydroxy \*\*\*thiol\*\*\* groups, sulfides, cyclic sulfides, molar ratio of cyclic sulfides to \*\*\*thiol\*\*\* groups, molar ratio of \*\*\*epoxide\*\*\* groups to \*\*\*thiol\*\*\* groups, molar ratio of \*\*\*epoxide\*\*\* groups to

.alpha.-hydroxy \*\*\*thiol\*\*\* groups, weight percent  
 \*\*\*thiol\*\*\* sulfur and other disclosed quantities of functional groups and their molar ratios as the epoxidized unsaturated ester composition. Thus, many of these properties will be discussed as an average number or ratio per hydroxy \*\*\*thiol\*\*\* ester molecule. In other embodiments, it is desired to control the content of \*\*\*thiol\*\*\* sulfur present in the hydroxy \*\*\*thiol\*\*\* ester. Because it is difficult to ensure that the hydrogen sulfide reacts with every \*\*\*epoxide\*\*\* group within the epoxidized unsaturated ester, certain hydroxy \*\*\*thiol\*\*\* ester molecules can have more or less \*\*\*thiol\*\*\* groups than other molecules within the hydroxy \*\*\*thiol\*\*\* ester composition. Thus, the weight percent of \*\*\*thiol\*\*\* groups can be stated as an average weight percent across all hydroxy \*\*\*thiol\*\*\* ester molecules.

DETD As an embodiment of the present invention, the hydroxy \*\*\*thiol\*\*\* ester composition includes hydroxy \*\*\*thiol\*\*\* ester molecules that have an average of at least 1 ester groups and an average of at least 1 .alpha.-hydroxy \*\*\*thiol\*\*\* groups per hydroxy \*\*\*thiol\*\*\* ester molecule. As an embodiment of the present invention, the hydroxy \*\*\*thiol\*\*\* ester composition includes hydroxy \*\*\*thiol\*\*\* ester molecules that have an average of at least 1.5 ester groups and an average of at least 1.5 .alpha.-hydroxy \*\*\*thiol\*\*\* groups per hydroxy \*\*\*thiol\*\*\* ester molecule.

DETD Minimally, in some embodiments, the hydroxy \*\*\*thiol\*\*\* ester comprises at least one ester, at least one \*\*\*thiol\*\*\* group, and at least one hydroxy group. Because the hydroxy \*\*\*thiol\*\*\* ester is prepared from epoxidized unsaturated esters, the hydroxy \*\*\*thiol\*\*\* ester can contain the same number of ester groups as the epoxidized unsaturated esters. In an embodiment, the hydroxy \*\*\*thiol\*\*\* ester molecules have an average of at least 1.5 ester groups per hydroxy \*\*\*thiol\*\*\* ester molecule. Alternatively, the hydroxy \*\*\*thiol\*\*\* ester molecules have an average of at least 2 ester groups per hydroxy \*\*\*thiol\*\*\* ester molecule; alternatively, an average of at

least 2.5  
 ester groups per hydroxy \*\*\*thiol\*\*\* ester molecule; or  
 alternatively, an average of at least 3 ester groups per hydroxy  
 \*\*\*thiol\*\*\* ester molecule. In other embodiments, the hydroxy  
 \*\*\*thiol\*\*\* esters have an average of from 1.5 to 8 ester  
 groups per  
 hydroxy \*\*\*thiol\*\*\* ester molecule; alternatively, an average  
 of  
 from 2 to 7 ester groups per hydroxy \*\*\*thiol\*\*\* ester  
 molecule;  
 alternatively, an average of from 2.5 to 5 ester groups per  
 hydroxy  
 \*\*\*thiol\*\*\* ester molecule; or alternatively, an average of  
 from 3 to  
 4 ester groups per hydroxy \*\*\*thiol\*\*\* ester molecule. In yet  
 other  
 embodiments, the .alpha.-hydroxy \*\*\*thiol\*\*\* ester comprises  
 an  
 average of 3 ester groups per hydroxy \*\*\*thiol\*\*\* ester  
 molecule or  
 alternatively, an average of 4 ester groups per hydroxy  
 \*\*\*thiol\*\*\*  
 ester molecule.  
 DETD In some embodiments, the hydroxy group and the \*\*\*thiol\*\*\*  
 group  
 are combined in the same group, which produces the .alpha.-  
 hydroxy  
 \*\*\*thiol\*\*\* group. In other embodiments, the \*\*\*thiol\*\*\*  
 group and  
 the hydroxy or alcohol group are not in the same group. When this  
 occurs, to produce the hydroxy \*\*\*thiol\*\*\* ester composition,  
 the  
 alcohol group is added independently of the \*\*\*thiol\*\*\*  
 group. For  
 example, as another embodiment of the present invention, the  
 hydroxy  
 \*\*\*thiol\*\*\* ester composition advantageously includes hydroxy  
 \*\*\*thiol\*\*\* ester molecules. The hydroxy \*\*\*thiol\*\*\*  
 ester  
 molecules have an average of at least 1.5 ester groups, an  
 average of at  
 least 1.5 \*\*\*thiol\*\*\* groups, and an average of at least 1.5  
 alcohol  
 groups per hydroxy \*\*\*thiol\*\*\* ester molecule.  
 DETD Minimally, in some embodiments, the hydroxy \*\*\*thiol\*\*\*  
 ester  
 comprises at least one \*\*\*thiol\*\*\* group per hydroxy  
 \*\*\*thiol\*\*\*  
 ester molecule. In an embodiment, the hydroxy \*\*\*thiol\*\*\*  
 ester  
 molecules have an average of at least 1.5 \*\*\*thiol\*\*\* groups  
 per  
 hydroxy \*\*\*thiol\*\*\* ester molecule; alternatively, an average  
 of at  
 least 2 \*\*\*thiol\*\*\* groups per hydroxy \*\*\*thiol\*\*\* ester  
 molecule; alternatively, an average of at least 2.5 \*\*\*thiol\*\*\*  
 groups per hydroxy \*\*\*thiol\*\*\* ester molecule; or  
 alternatively, an  
 average of at least 3 \*\*\*thiol\*\*\* groups per hydroxy  
 \*\*\*thiol\*\*\*



ester molecule. In other embodiments, the hydroxy \*\*\*thiol\*\*\* ester molecules have an average of from 1.5 to 9 \*\*\*thiol\*\*\* groups per hydroxy \*\*\*thiol\*\*\* ester molecule; alternatively, an average of from 3 to 8 \*\*\*thiol\*\*\* groups per hydroxy \*\*\*thiol\*\*\* ester molecule; alternatively, an average of from 2 to 4 \*\*\*thiol\*\*\* groups per hydroxy \*\*\*thiol\*\*\* ester molecule; or alternatively, an average of from 4 to 8 \*\*\*thiol\*\*\* groups per hydroxy \*\*\*thiol\*\*\* ester.

DETD Minimally, in some embodiments, the hydroxy \*\*\*thiol\*\*\* ester composition comprises an average of at least 1 hydroxy or alcohol group per hydroxy \*\*\*thiol\*\*\* ester molecule. In some embodiments, the hydroxy \*\*\*thiol\*\*\* ester composition comprises an average of at least 1.5 hydroxy groups per hydroxy \*\*\*thiol\*\*\* ester molecule; alternatively, average of at least 2 hydroxy groups per hydroxy \*\*\*thiol\*\*\* ester molecule; alternatively, an average of at least 2.5

hydroxy groups per hydroxy \*\*\*thiol\*\*\* ester molecule; or alternatively, an average of at least 3 hydroxy groups per \*\*\*thiol\*\*\* ester molecule. In other embodiments, the \*\*\*thiol\*\*\* ester composition comprises an average of from 1.5 to 9 hydroxy groups per hydroxy \*\*\*thiol\*\*\* ester molecule; alternatively, an average of from 3 to 8 hydroxy groups per hydroxy \*\*\*thiol\*\*\* ester molecule; alternatively, an average of from 2 to 4 hydroxy groups per hydroxy \*\*\*thiol\*\*\* ester molecule; or alternatively, an average of from 4 to 8 hydroxy groups per hydroxy \*\*\*thiol\*\*\* ester molecule.

DETD In yet other embodiments, the number of hydroxy groups can be stated as

an average molar ratio of hydroxy group to \*\*\*thiol\*\*\* groups.

Minimally, in some embodiments, the molar ratio of hydroxy groups to

\*\*\*thiol\*\*\* groups is at least 0.25. In some embodiments, the molar ratio of hydroxy groups to \*\*\*thiol\*\*\* groups is at least 0.5;

alternatively, at least 0.75; alternatively, at least 1.0; alternatively, at least 1.25; or alternatively, at least 1.5. In

other embodiments, the molar ratio of hydroxy groups to \*\*\*thiol\*\*\* groups ranges from 0.25 to 2.0; alternatively, from 0.5 to 1.5; or alternatively, from 0.75 to 1.25.

DETD In embodiments where the hydroxy \*\*\*thiol\*\*\* esters are

produced from an epoxidized unsaturated ester, the hydroxy **thiol** esters can be described as containing ester groups and  $\alpha$ -hydroxy **thiol** groups. The number of ester groups and the number of  $\alpha$ -hydroxy **thiol** groups are independent elements and as such the hydroxy **thiol** esters can be described as having any combination of ester groups and  $\alpha$ -hydroxy **thiol** groups described herein. Minimally, the hydroxy **thiol** ester comprises an average of at least 1  $\alpha$ -hydroxy **thiol** group per hydroxy **thiol** ester molecule. In some embodiments, the hydroxy **thiol** ester composition comprises an average of at least 1.5  $\alpha$ -hydroxy **thiol** groups per hydroxy **thiol** ester molecule; alternatively, an average of at least 2  $\alpha$ -hydroxy **thiol** groups per hydroxy **thiol** ester molecule; alternatively, an average of at least 2.5  $\alpha$ -hydroxy **thiol** groups per hydroxy **thiol** ester molecule; or alternatively, an average of at least 3  $\alpha$ -hydroxy **thiol** groups per hydroxy **thiol** ester molecule. In other embodiments, the hydroxy **thiol** ester composition comprises an average of from 1.5 to 9  $\alpha$ -hydroxy **thiol** groups per hydroxy **thiol** ester molecule; alternatively, an average of from 3 to 8  $\alpha$ -hydroxy **thiol** groups per hydroxy **thiol** ester molecule; alternatively, an average of from 2 to 4  $\alpha$ -hydroxy **thiol** groups per hydroxy **thiol** ester molecule; or alternatively, an average of from 4 to 8  $\alpha$ -hydroxy **thiol** groups per hydroxy **thiol** ester molecule.

DETD The hydroxy **thiol** esters can be produced by contacting an epoxidized ester derived from an unsaturated ester (i.e., epoxidized unsaturated ester), as described herein. In some instances it can be desirable to have **epoxide** groups present in the hydroxy **thiol** ester composition. While in other embodiments, it can be desirable to minimize the number of epoxy groups present in the hydroxy **thiol** ester composition. Thus, the presence of residual **epoxide** groups can be another separate functional group used to describe the hydroxy **thiol** ester.

DETD The presence of \*\*\*epoxide\*\*\* groups in the hydroxy  
 \*\*\*thiol\*\*\*  
 ester can be independently described as an average number of  
 \*\*\*epoxide\*\*\* groups per hydroxy \*\*\*thiol\*\*\* ester, a  
 molar ratio  
 of \*\*\*epoxide\*\*\* groups to \*\*\*thiol\*\*\* groups, a molar  
 ratio of  
 \*\*\*epoxide\*\*\* groups to .alpha.-hydroxy \*\*\*thiol\*\*\*  
 groups, or any  
 combination thereof. In some embodiments, the hydroxy  
 \*\*\*thiol\*\*\*  
 ester molecules comprise an average of less than 2  
 \*\*\*epoxide\*\*\*  
 groups per hydroxy \*\*\*thiol\*\*\* ester molecule, i.e., the  
 hydroxy  
 \*\*\*thiol\*\*\* ester molecules have a molar ratio of  
 \*\*\*epoxide\*\*\*  
 groups to .alpha.-hydroxy \*\*\*thiol\*\*\* groups of less than 2.  
 Alternatively, the hydroxy \*\*\*thiol\*\*\* ester comprises an  
 average of  
 less than 1.5 \*\*\*epoxide\*\*\* groups per hydroxy \*\*\*thiol\*\*\*  
 ester  
 molecule; alternatively, an average of less than 1  
 \*\*\*epoxide\*\*\*  
 group per hydroxy \*\*\*thiol\*\*\* ester molecule; alternatively,  
 an  
 average of less than 0.75 \*\*\*epoxide\*\*\* groups per hydroxy  
 \*\*\*thiol\*\*\* ester molecule; or alternatively, an average of  
 less than  
 0.5 \*\*\*epoxide\*\*\* groups per hydroxy \*\*\*thiol\*\*\* ester  
 molecule.  
 In other embodiments, the molar ratio of \*\*\*epoxide\*\*\* groups  
 to  
 \*\*\*thiol\*\*\* groups averages less than 1.5. Alternatively, the  
 molar  
 ratio of \*\*\*epoxide\*\*\* groups to \*\*\*thiol\*\*\* groups  
 averages  
 less than 1; alternatively, averages less than 0.75;  
 alternatively,  
 averages less than 0.5; alternatively, averages less than 0.25;  
 or  
 alternatively, averages less than 0.1. In yet other embodiments,  
 the  
 molar ratio of \*\*\*epoxide\*\*\* groups to .alpha.-hydroxy  
 \*\*\*thiol\*\*\*  
 groups averages less than 1.5. Alternatively, the molar ratio of  
 \*\*\*epoxide\*\*\* groups to .alpha.-hydroxy \*\*\*thiol\*\*\*  
 groups  
 averages less than 1; alternatively, averages less than 0.75;  
 alternatively, averages less than 0.5; alternatively, averages  
 less than  
 0.25; or alternatively, averages less than 0.1.  
 DETD In some embodiments, the hydroxy \*\*\*thiol\*\*\* ester  
 composition is  
 substantially free of \*\*\*epoxide\*\*\* groups.  
 DETD In other embodiments, the hydroxy \*\*\*thiol\*\*\* ester can be  
 described by the average amount of \*\*\*thiol\*\*\* sulfur present  
 in  
 hydroxy \*\*\*thiol\*\*\* ester. In an embodiment, the hydroxy  
 \*\*\*thiol\*\*\* ester molecules have an average of at least 2.5

weight  
percent \*\*\*thiol\*\*\* sulfur per hydroxy \*\*\*thiol\*\*\* ester  
molecule; alternatively, an average of at least 5 weight percent  
\*\*\*thiol\*\*\* sulfur per hydroxy \*\*\*thiol\*\*\* ester  
molecule;  
alternatively, an average of at least 10 weight percent  
\*\*\*thiol\*\*\*  
sulfur per hydroxy \*\*\*thiol\*\*\* ester molecule; or  
alternatively, an  
average of greater than 15 weight percent \*\*\*thiol\*\*\* sulfur  
per  
hydroxy \*\*\*thiol\*\*\* ester molecule. In an embodiment, the  
hydroxy  
\*\*\*thiol\*\*\* ester molecules have an average of from 5 to 25  
weight  
percent \*\*\*thiol\*\*\* sulfur per hydroxy \*\*\*thiol\*\*\* ester  
molecule; alternatively, an average of from 5 to 20 weight  
percent  
\*\*\*thiol\*\*\* sulfur per hydroxy \*\*\*thiol\*\*\* ester  
molecule;  
alternatively, an average of from 6 to 15 weight percent  
\*\*\*thiol\*\*\*  
sulfur per hydroxy \*\*\*thiol\*\*\* ester molecule; or  
alternatively, an  
average of from 8 to 10 weight percent \*\*\*thiol\*\*\* sulfur per  
hydroxy \*\*\*thiol\*\*\* ester molecule.  
DETD In some embodiments, at least 20 percent of the total side  
chains  
include the .alpha.-hydroxy \*\*\*thiol\*\*\* group. In some  
embodiments,  
at least 20 percent of the total side chains include the .alpha.-  
hydroxy  
\*\*\*thiol\*\*\* group. In some embodiments, at least 60 percent  
of the  
total side chains include the .alpha.-hydroxy \*\*\*thiol\*\*\*  
group;  
alternatively, at least 70 percent of the total side chains  
include the  
.alpha.-hydroxy \*\*\*thiol\*\*\* group. Yet in other embodiments,  
at  
least 80 percent of the total side chains include the .alpha.-  
hydroxy  
\*\*\*thiol\*\*\* group.  
DETD In some aspects, greater than 20 percent of the hydroxy  
\*\*\*thiol\*\*\*  
ester molecule total side chains contain sulfur. In some aspects,  
greater than 40 percent of the hydroxy \*\*\*thiol\*\*\* ester  
molecule  
total side chains contain sulfur. In some aspects, greater than  
60  
percent of the hydroxy \*\*\*thiol\*\*\* ester molecule total side  
chains  
contain sulfur; alternatively, greater than 70 percent of the  
total side  
chains contain sulfur; or alternatively, greater than 80 percent  
of the  
total side chains contain sulfur.  
DETD In particular embodiments, the epoxidized unsaturated ester used  
in the  
synthesis of the hydroxy \*\*\*thiol\*\*\* ester is produced from

the epoxidized unsaturated ester composition that includes an epoxidized natural source oil. Because the natural source oils have particular compositions regarding the number of ester groups present, the hydroxy \*\*\*thiol\*\*\* ester will have about the same number of ester groups as the feedstock natural source oil. Other independent properties that are described herein can be used to further describe the hydroxy \*\*\*thiol\*\*\* ester.

DETD In other embodiments, the epoxidized unsaturated ester used to produce the hydroxy \*\*\*thiol\*\*\* ester is produced from synthetic (or semi-synthetic) unsaturated ester oils. Because the synthetic ester oils can have particular compositions regarding the number of ester groups present, the hydroxy \*\*\*thiol\*\*\* ester would have about the same number of ester groups as the synthetic ester oil. Other, independent properties of the unsaturated ester, whether the unsaturated ester includes natural source or synthetic oils, can be used to further describe the hydroxy \*\*\*thiol\*\*\* ester composition.

DETD The hydroxy \*\*\*thiol\*\*\* ester compositions can also be described as a product produced by the process comprising contacting hydrogen sulfide and an epoxidized unsaturated ester composition and can be further limited by the process as described herein. The hydroxy \*\*\*thiol\*\*\* containing natural source oil can also be described using an average molecular weight or an average molecular weight of the side chains.

DETD Cross-Linked \*\*\*Thiol\*\*\* Ester Compositions

DETD In an aspect, the present invention relates to a cross-linked \*\*\*thiol\*\*\* ester composition. Generally, the cross-linked \*\*\*thiol\*\*\* ester molecules are oligomers of \*\*\*thiol\*\*\* esters that are connected together by polysulfide linkages --S.sub.x-- wherein x is an integer greater 1. As the cross-linked \*\*\*thiol\*\*\* ester is described as an oligomer of \*\*\*thiol\*\*\* esters, the \*\*\*thiol\*\*\* esters can be described as the monomer from which the cross-linked \*\*\*thiol\*\*\* esters are produced.

DETD In an aspect, the cross-linked \*\*\*thiol\*\*\* ester composition comprises a \*\*\*thiol\*\*\* ester oligomer having at least two \*\*\*thiol\*\*\* ester monomers connected by a polysulfide linkage having a structure --S.sub.Q--, wherein Q is an integer greater than 1. In an

aspect, the polysulfide linkage may be the polysulfide linkage --S.sub.Q--, wherein Q is 2, 3, 4, or mixtures thereof. In other embodiments, Q can be 2; alternatively, 3; or alternatively, 4.

DETD In an aspect, the cross-linked \*\*\*thiol\*\*\* ester composition comprises a \*\*\*thiol\*\*\* ester oligomer having at least 3 \*\*\*thiol\*\*\* ester monomers connected by polysulfide linkages; alternatively, 5 \*\*\*thiol\*\*\* ester monomers connected by polysulfide linkages; alternatively, 7 \*\*\*thiol\*\*\* ester monomers connected by polysulfide linkages; or alternatively, 10 \*\*\*thiol\*\*\* ester monomers connected by polysulfide linkages. In yet other embodiments, the cross-linked \*\*\*thiol\*\*\* ester composition comprises a \*\*\*thiol\*\*\* ester oligomer having from 3 to 20 \*\*\*thiol\*\*\* ester monomers connected by polysulfide linkages; alternatively, from 5 to 15 \*\*\*thiol\*\*\* ester monomers connected by polysulfide linkages; or alternatively, from 7 to 12 \*\*\*thiol\*\*\* ester monomers connected by polysulfide linkages.

DETD In an aspect, the cross-linked \*\*\*thiol\*\*\* ester composition comprises \*\*\*thiol\*\*\* ester monomers and \*\*\*thiol\*\*\* ester oligomers. In some embodiments, the cross-linked \*\*\*thiol\*\*\* ester composition has a combined \*\*\*thiol\*\*\* ester monomer and \*\*\*thiol\*\*\* ester oligomer average molecular weight greater than 2,000. In other embodiments, the cross-linked \*\*\*thiol\*\*\* ester composition has a combined \*\*\*thiol\*\*\* ester monomer and \*\*\*thiol\*\*\* ester oligomer average molecular weight greater than 5,000; or alternatively, greater than 10,000. In yet other embodiments, the cross-linked \*\*\*thiol\*\*\* ester composition has a combined \*\*\*thiol\*\*\* ester monomer and \*\*\*thiol\*\*\* ester oligomer average molecular weight ranging from 2,000 to 20,000; alternatively, from 3,000 to 15,000; or alternatively, from 7,500 to 12,500.

DETD In an aspect, the \*\*\*thiol\*\*\* ester monomers and \*\*\*thiol\*\*\* ester oligomers have a total \*\*\*thiol\*\*\* sulfur content greater than 0.5. In other embodiments, the \*\*\*thiol\*\*\* ester monomers and \*\*\*thiol\*\*\* ester oligomers have a total \*\*\*thiol\*\*\* sulfur content greater than 1; alternatively, greater than 2; alternatively, greater than 4. In yet other embodiments, the \*\*\*thiol\*\*\* ester monomers and the \*\*\*thiol\*\*\* ester oligomers have a total \*\*\*thiol\*\*\* sulfur content from 0.5 to 8; alternatively, from 4 to 8; or alternatively, 0.5 to 4.

DETD In an aspect, the \*\*\*thiol\*\*\* ester monomers and

\*\*\*thiol\*\*\*  
ester oligomers have a total sulfur content greater than 8. In  
some  
embodiments, the \*\*\*thiol\*\*\* ester monomers and \*\*\*thiol\*\*\*  
ester oligomers have a total sulfur content greater than 10;  
alternatively, greater than 12. In yet other embodiments, the  
\*\*\*thiol\*\*\* ester monomers and \*\*\*thiol\*\*\* ester  
oligomers have a  
total sulfur content ranging from 8 to 15 weight percent;  
alternatively,  
from 9 to 14; or alternatively, from 10 to 13.  
DETD The cross-linked \*\*\*thiol\*\*\* ester compositions can also be  
described as a product produced by the process comprising  
contacting a  
\*\*\*thiol\*\*\* ester with oxidizing agent and can be further  
limited by  
the process as described herein.  
DETD The present invention advantageously includes sulfide-containing  
ester  
compositions as embodiments of the present invention. Generally,  
the  
sulfide-containing ester compositions can be described as  
containing  
molecules having at least one ester group and a least one sulfide  
group  
within each molecule. The sulfide-containing esters used in the  
present  
invention can be produced by contacting either an unsaturated  
ester or  
an epoxidized unsaturated ester with a \*\*\*thiol\*\*\* containing  
compound as described herein.  
DETD The feedstock unsaturated esters can contain multiple carbon-  
carbon  
double bonds per unsaturated ester molecule. The carbon-carbon  
double  
bond reactivity and statistical probability, however, dictate  
that each  
sulfide-containing ester molecule of the \*\*\*thiol\*\*\* -  
containing  
ester composition produced from the unsaturated ester composition  
will  
not have the same number of sulfide groups, number of unreacted  
carbon-carbon double bonds, molar ratio of carbon-carbon double  
bonds to  
sulfide groups, molar ratio of cyclic sulfides to \*\*\*thiol\*\*\*  
groups  
and other herein disclosed quantities of functional groups and  
molar  
ratios. Additionally, the feedstock unsaturated esters can also  
comprise  
a mixture of individual unsaturated esters having a different  
number of  
carbon-carbon double bonds and/or ester groups. Many of these  
properties  
are discussed herein as an average number of the groups per  
sulfide-containing ester molecule within the sulfide-containing  
ester  
composition or average ratio per \*\*\*thiol\*\*\* -containing ester  
molecule within the sulfide-containing ester composition.  
DETD In embodiments related to the sulfide-containing ester that is

produced from an epoxidized unsaturated ester, the feedstock epoxidized unsaturated esters can contain multiple \*\*\*epoxide\*\*\* groups per unsaturated ester molecule. Individual \*\*\*epoxide\*\*\* group reactivity and statistical probability dictate that each sulfide-containing ester molecule of the sulfide-containing ester composition produced from the unsaturated ester composition will not have the same number of sulfide groups, number of unreacted \*\*\*epoxide\*\*\* groups, molar ratio of \*\*\*epoxide\*\*\* groups to sulfide groups, and other herein disclosed quantities of functional groups and molar ratios. Additionally, the feedstock epoxidized unsaturated esters can also comprise a mixture of individual epoxidized unsaturated ester molecules having a different number of \*\*\*epoxide\*\*\* groups and/or ester groups. Thus, many of these properties are described as an average number of the groups per sulfide-containing ester molecules within the sulfide-containing ester composition or average ratio per \*\*\*thiol\*\*\* -containing ester molecule within the sulfide-containing ester composition.

DETD Minimally, in some embodiments, the sulfide-containing esters comprise at least one ester group per sulfide-containing ester molecule. In some embodiments, the sulfide-containing ester has an average of at least 1.5 ester groups per sulfide-containing ester molecule. Alternatively, the sulfide-containing ester molecules have an average of at least 2 ester groups per sulfide-containing ester molecule; alternatively, an average of at least 2.5 ester groups per sulfide-containing ester molecule; or alternatively, an average of at least 3 ester groups per sulfide-containing ester molecule. In other embodiments, the sulfide-containing esters have an average of from 1.5 to 9 ester groups per sulfide-containing ester molecule; alternatively, an average of from 1.5 to 8 ester groups per sulfide-containing ester molecule; alternatively, an average of from 2 to 8 ester groups per sulfide-containing ester molecule; alternatively, an average of from 2 to 7 ester groups per sulfide-containing ester molecule; alternatively, an average of from 2.5 to 5 ester groups per sulfide-containing ester molecule; alternatively, an average of from 3 to 5 ester groups per sulfide-containing ester molecule; or alternatively, an average of from 3 to 4 ester groups per sulfide-containing ester molecule. In yet other



embodiments, the hydroxy \*\*\*thiol\*\*\* -containing ester comprises an average of about 3 ester groups per sulfide-containing ester molecule; or alternatively, an average of about 4 ester groups per sulfide-containing ester molecule.

DETD In some embodiments, R.sup.3 comprises at least one functional group. In one aspect, the functional group is selected from the group consisting of a hydroxy group, a carboxylic acid group, a carboxylic ester group, an amine group, a sulfide group, and a second \*\*\*thiol\*\*\* group. In some aspects, R.sup.3 comprises at least two functional groups. In some aspects, the functional groups are selected from the group consisting of a hydroxy group, carboxylic acid group, a carboxylic ester group, an amine group, a sulfide group, a second \*\*\*thiol\*\*\* group, and mixtures thereof.

DETD The sulfide-containing ester compositions can also be described as a product produced by the process comprising contacting an unsaturated ester with a \*\*\*mercaptan\*\*\* and can be further limited by the process as described herein. In other embodiments, the sulfide-containing ester composition can also be described as a product produced by a process comprising contacting an epoxidized unsaturated ester with a \*\*\*mercaptan\*\*\* and can be further limited by the process as described herein.

DETD Generally, the thioacrylate ester composition can be described as comprising thioacrylate molecules having at least one ester group in addition to any acrylate or thioacrylate ester groups present in the thioacrylate molecule and at least one thioacrylate group. The ester group(s) that are in addition to any acrylate or thioacrylate ester groups present in the thioacrylate molecule are hereinafter referred to as "supplementary ester group(s)." The thioacrylate ester composition described herein can be produced by contacting an acrylate composition with a \*\*\*thiol\*\*\* -containing ester composition and/or a hydroxy \*\*\*thiol\*\*\* -containing ester composition, both of which are described herein.

DETD The feedstock \*\*\*thiol\*\*\* ester compositions and/or hydroxy \*\*\*thiol\*\*\* ester compositions can comprise a mixture of molecules that have an average quantity of ester groups, \*\*\*thiol\*\*\*

groups,  
hydroxy groups, and other groups and molar ratios described  
herein.  
Additionally, individual \*\*\*thiol\*\*\* and hydroxy group  
reactivity  
within the \*\*\*thiol\*\*\* -containing ester compositions and/or  
hydroxy  
\*\*\*thiol\*\*\* ester compositions and statistical probability  
dictate  
that each thioacrylate ester molecule of the thioacrylate ester  
composition produced may not have the same number of ester  
groups,  
thioacrylate groups, acrylate groups, and other herein disclosed  
quantities of functional groups, moieties, and molar ratios.  
Thus, many  
of the properties of the thioacrylate ester molecules within the  
thioacrylate ester composition are described as using an average  
number  
of the groups per thioacrylate ester molecule within the  
thioacrylate  
ester composition or as an average ratio per thioacrylate ester  
molecule  
within the thioacrylate ester composition.  
DETD The thioacrylate ester can also be described as a product  
produced by  
the process that includes contacting a \*\*\*thiol\*\*\* -containing  
ester  
composition with an acrylate composition and can be further  
limited by  
the process described herein. In other embodiments, the  
thioacrylate  
ester composition can also be described as a product produced by  
a  
process that includes contacting a hydroxy \*\*\*thiol\*\*\* -  
containing  
ester composition with an acrylate composition and can be further  
limited by the process described herein.  
DETD The present invention advantageously provides a sulfonic  
acid-containing ester as an embodiment of the present invention.  
Generally, the sulfonic acid-containing ester of the present  
invention  
includes sulfonic acid-containing ester molecules having at least  
one  
ester group and a least one sulfonic acid group. The sulfonic  
acid-containing ester described herein can be produced by  
contacting a  
\*\*\*thiol\*\*\* ester with an oxidizing agent as described  
herein. Because  
the feedstock for the production of the sulfonic acid-containing  
ester  
can include multiple \*\*\*thiols\*\*\* groups, \*\*\*thiol\*\*\*  
group  
reactivity and statistical probability dictate that each sulfonic  
acid-containing ester molecule of the sulfonic acid-containing  
ester  
will not have the same number of sulfonic acid groups.  
Additionally, the  
feedstock \*\*\*thiol\*\*\* ester can also include a mixture of  
individual  
\*\*\*thiol\*\*\* ester molecules having different numbers of

\*\*\*thiol\*\*\*

groups and/or ester groups. Thus, many of the groups present in the sulfonic acid-containing ester are described herein as an average number of the groups per sulfonic acid-containing ester molecule or an average ratio per sulfonic acid-containing ester molecule within the sulfonic acid-containing ester.

DETD In some embodiments of the present invention, the sulfonic acid ester is substantially free of \*\*\*thiol\*\*\* groups.

DETD The sulfonic acid-containing ester can also be described as a product produced by the process comprising contacting a \*\*\*thiol\*\*\* ester with an oxidizing agent described herein.

DETD Process for Making a \*\*\*Thiol\*\*\* Ester Composition

DETD The present invention advantageously provides processes for producing a \*\*\*thiol\*\*\* ester composition as embodiments of the present invention.

As an embodiment, the present invention advantageously includes a process to produce a \*\*\*thiol\*\*\* ester composition by contacting hydrogen sulfide and an unsaturated ester composition containing unsaturated esters and reacting the hydrogen sulfide and unsaturated esters to form or produce the \*\*\*thiol\*\*\* ester composition.

As another embodiment of the present invention, a process to produce the \*\*\*thiol\*\*\* ester composition is advantageously provided. In this embodiment, the process includes contacting a composition

comprising a polyol with a composition comprising a \*\*\*thiol\*\*\* containing carboxylic acid composition and reacting the polyol and \*\*\*thiol\*\*\* containing carboxylic acid composition to form the \*\*\*thiol\*\*\* ester composition.

DETD In some embodiments of the present invention that include producing \*\*\*thiol\*\*\* ester compositions, the unsaturated ester composition is a

natural source oil. In an aspect, the unsaturated ester composition is soybean oil or alternatively castor oil. Other suitable types of unsaturated ester compositions are described herein and can be used in the processes for producing the \*\*\*thiol\*\*\* ester compositions.

DETD \*\*\*Thiol\*\*\* Esters from Unsaturated Esters

DETD As an embodiment of the present invention, the \*\*\*thiol\*\*\* esters described herein can be produced by a process comprising contacting hydrogen sulfide and an unsaturated ester composition and

reacting hydrogen sulfide and the unsaturated ester composition to form the **thiol** ester composition. In one embodiment, the unsaturated ester composition includes unsaturated esters having an average of at least 1.5 ester groups and an average of at least 1.5 carbon-carbon double bonds per unsaturated ester molecule. In this embodiment, the **thiol** ester composition includes **thiol** ester molecules having a molar ratio of cyclic sulfides to **thiol** groups of less than 1.5.

DETD The processes for producing the **thiol** ester composition can be applied to any of the unsaturated esters described herein and used to produce any of the **thiol** esters described herein. The process for producing the **thiol** ester composition can also include any additional process steps or process conditions described herein.

DETD The hydrogen sulfide to molar equivalents of unsaturated ester carbon-carbon double bonds molar ratio utilized in the process to produce the **thiol** ester composition can be any molar ratio that produces the desired **thiol** ester. The molar equivalents of unsaturated ester carbon-carbon double bonds is calculated by the equation: 
$$\frac{UES\ GMW}{UES\ Mass} \times \frac{UES\ C.dbd.C}{UES\ C.dbd.C}$$
 In this equation, UES GMW is the average gram molecular weight of the unsaturated ester, UES Mass is the mass of the feedstock unsaturated ester, and UES C.dbd.C is the average number of double bonds per unsaturated ester molecule. In some embodiments, the **thiol** ester molecules have a molar ratio of the hydrogen sulfide to the unsaturated ester carbon-carbon double bonds of greater than 2. In other embodiments, the hydrogen sulfide to unsaturated ester carbon-carbon double bonds molar ratio is greater than 5; alternatively, greater than 10; alternatively, greater than 15; or alternatively, greater than 20. In other embodiments, the hydrogen sulfide to unsaturated ester carbon-carbon double bonds molar ratio can be from 2 to 500; alternatively, from 5 to 200; alternatively, from 10 to 100; or alternatively, from 100 to 200.

DETD When a continuous reactor is used, a feed unsaturated ester weight hourly space velocity ranging from 0.1 to 5 can be used to produce the

desired \*\*\*thiol\*\*\* ester. Alternatively, the feed unsaturated ester weight hourly space velocity ranges between 0.1 to 5; alternatively, from 0.1 to 2. Alternatively, the feed unsaturated ester weight hourly space velocity is 0.1; alternatively, the feed unsaturated ester weight hourly space velocity is 0.25; or alternatively, the feed unsaturated ester weight hourly space velocity is 2.

DETD The time required for the reaction of the unsaturated ester and hydrogen sulfide can be any time required to form the described \*\*\*thiol\*\*\* ester. Generally, the time required for the reaction of the unsaturated ester and hydrogen sulfide is at least 5 minutes.

In some embodiments, the time required for the reaction of the unsaturated ester and hydrogen sulfide ranges from 5 minutes to 72 hours; alternatively, from 10 minutes to 48 hours; or alternatively, from 15 minutes to 36 hours.

DETD In embodiments, the process to produce the \*\*\*thiol\*\*\* ester further comprises a step to remove excess or residual hydrogen sulfide after reacting the hydrogen sulfide and the unsaturated ester composition. In some embodiments, the \*\*\*thiol\*\*\* ester is vacuum stripped. In some embodiments, the \*\*\*thiol\*\*\* ester is vacuum stripped at a temperature ranging between 25.degree. C. and 250.degree. C.; or alternatively, between 50.degree. C. and 200.degree. C. In other embodiments, the \*\*\*thiol\*\*\* ester is sparged with an inert gas to remove hydrogen sulfide. In some embodiments, the \*\*\*thiol\*\*\* ester is sparged with an inert gas at a temperature between 25.degree. C. and 250.degree. C.; or alternatively, between 50.degree. C. and 200.degree. C. In some aspects, the inert gas is nitrogen. Generally, the stripped or sparged \*\*\*thiol\*\*\* ester comprises less than 0.1 weight percent hydrogen sulfide. In other embodiments, the stripped or sparged \*\*\*thiol\*\*\* ester comprises less than 0.05 weight percent sulfur; alternatively, less than 0.025 weight percent hydrogen sulfide; or alternatively, less than 0.01 weight percent hydrogen sulfide

DETD The reaction between the unsaturated ester and hydrogen sulfide can be performed at any temperature capable of forming the \*\*\*thiol\*\*\* ester. In some embodiments, the unsaturated ester and hydrogen sulfide can be reacted at a temperature greater than -20.degree. C. In other

embodiments, the unsaturated ester and hydrogen sulfide can be reacted

at a temperature greater than 0.degree. C.; alternatively, greater than

20.degree. C.; alternatively, greater than 50.degree. C.; alternatively,

greater than 80.degree. C.; or alternatively, greater than 100.degree.

C. In yet other embodiments, the unsaturated ester and hydrogen sulfide

can be reacted at a temperature from -20.degree. C. to 200.degree. C.;

alternatively, from 120.degree. C. to 240.degree. C.; alternatively,

from 170.degree. C. to 210.degree. C.; alternatively, from 185.degree.

C. to 195.degree. C.; alternatively, from 20.degree. C. to 200.degree.

C.; alternatively, from 20.degree. C. to 170.degree. C.; or alternatively, from 80.degree. C. to 140.degree. C.

DETD \*\*\*Thiol\*\*\* esters having a low cyclic sulfide content can be

produced using the disclosed process. In an aspect, the process for

producing the \*\*\*thiol\*\*\* ester forms or produces a \*\*\*thiol\*\*\*

ester having a molar ratio of cyclic sulfide to \*\*\*thiol\*\*\*

groups of less than 1.5. Additional cyclic sulfide to \*\*\*thiol\*\*\*

groups molar ratios are disclosed herein.

DETD In addition to lower cyclic sulfide content, \*\*\*thiol\*\*\* esters

having a low carbon-carbon double bond to \*\*\*thiol\*\*\* group

molar ratio can also be produced using the disclosed process. In an

aspect, the process described herein produces the \*\*\*thiol\*\*\* ester

having a carbon-carbon double bond to \*\*\*thiol\*\*\* group molar ratio of

less than 1.5. Additional carbon-carbon double bond to \*\*\*thiol\*\*\*

group molar ratios are disclosed herein.

DETD In some aspects, the process described herein produces the \*\*\*thiol\*\*\* ester molecules having an average of greater than 5 weight

percent \*\*\*thiol\*\*\* sulfur. Additional \*\*\*thiol\*\*\* sulfur contents are disclosed herein. In other aspects, the process for producing a \*\*\*thiol\*\*\* ester forms a \*\*\*thiol\*\*\* ester

having greater than 40 percent of the \*\*\*thiol\*\*\* ester total side

chains include sulfur. Other percentages of the \*\*\*thiol\*\*\* ester

total side chains that include sulfur are disclosed herein.

DETD In some embodiments, the process for producing a \*\*\*thiol\*\*\* ester

composition includes contacting an unsaturated ester and hydrogen sulfide and reacting the unsaturated ester and the hydrogen

sulfide to form a \*\*\*thiol\*\*\* ester. The \*\*\*thiol\*\*\* ester comprises \*\*\*thiol\*\*\* ester molecules that have a ratio of cyclic sulfide to \*\*\*thiol\*\*\* groups of less than 1.5.

DETD \*\*\*Thiol\*\*\* Ester from a Polyol and a \*\*\*Thiol\*\*\* Containing Carboxylic Acid Derivative

DETD As another embodiment of the present invention, another process to produce the \*\*\*thiol\*\*\* ester composition is advantageously provided. In this embodiment, the process includes the steps of contacting a composition comprising a polyol with a composition comprising a \*\*\*thiol\*\*\* containing carboxylic acid and/or \*\*\*thiol\*\*\* containing carboxylic acid derivative and reacting the polyol and \*\*\*thiol\*\*\* containing carboxylic acid and/or \*\*\*thiol\*\*\* containing carboxylic acid derivative to produce the \*\*\*thiol\*\*\* ester composition. This process can be applied to any polyol, \*\*\*thiol\*\*\* containing carboxylic acid, or \*\*\*thiol\*\*\* containing carboxylic acid derivative described herein. The process for producing the \*\*\*thiol\*\*\* ester composition can also include any additional process steps or process conditions described herein. Additionally, the process for producing the \*\*\*thiol\*\*\* ester composition can form any \*\*\*thiol\*\*\* ester described herein.

DETD In some embodiments, the \*\*\*thiol\*\*\* ester composition includes \*\*\*thiol\*\*\* ester molecules that have an average of at least 1.5 ester groups and an average of at least 1.5 \*\*\*thiol\*\*\* groups per \*\*\*thiol\*\*\* ester molecule.

DETD The polyol used to produce the \*\*\*thiol\*\*\* ester by contacting a polyol and a \*\*\*thiol\*\*\* carboxylic acid and/or \*\*\*thiol\*\*\* carboxylic acid equivalent (for example a \*\*\*thiol\*\*\* carboxylic acid methyl ester) can be any polyol or mixture of polyols that can produce the described \*\*\*thiol\*\*\* containing ester.

DETD In one aspect, the polyol used to produce the \*\*\*thiol\*\*\* ester can comprise from 2 to 20 carbon atoms. In other embodiments, the polyol comprises from 2 to 10 carbon atoms; alternatively from 2 to 7 carbon atoms; alternatively from 2 to 5 carbon atoms. In further embodiments, the polyol may be a mixture of polyols having an average of 2 to 20 carbon atoms; alternatively, an average of from 2 to 10 carbon atoms; alternatively, an average of 2 to 7 carbon atoms; alternatively an average of 2 to 5 carbon atoms.

DETD In another aspect, the polyol used to produce the \*\*\*thiol\*\*\*

ester

can have any number of hydroxy groups needed to produce the  
\*\*\*thiol\*\*\* ester as described herein. In some embodiments,  
the polyol  
has 2 hydroxy groups; alternatively 3 hydroxy groups;  
alternatively, 4  
hydroxy groups; alternatively, 5 hydroxy groups; or  
alternatively, 6  
hydroxy groups. In other embodiments, the polyol comprises at  
least 2  
hydroxy groups; alternatively at least 3 hydroxy groups;  
alternatively,  
at least 4 hydroxy groups; or alternatively, at least 5 hydroxy  
groups;  
at least 6 hydroxy groups. In yet other embodiments, the polyol  
comprises from 2 to 8 hydroxy groups; alternatively, from 2 to 4  
hydroxy  
groups; or alternatively from 4 to 8 hydroxy groups.

DETD In further aspects, the polyol used to produce the \*\*\*thiol\*\*\*  
ester is a mixture of polyols. In an embodiment, the mixture of  
polyols

has an average of at least 1.5 hydroxy groups per polyol  
molecule. In  
other embodiments, the mixture of polyols has an average of at  
least 2  
hydroxy groups per polyol molecule; alternatively, an average of  
at  
least 2.5 hydroxy groups per polyol molecule; alternatively, an  
average  
of at least 3.0 hydroxy groups per polyol molecule; or  
alternatively, an  
average of at least 4 hydroxy groups per polyol molecule. In yet  
another  
embodiments, the mixture of polyols has an average of 1.5 to 8  
hydroxy  
groups per polyol molecule; alternatively, an average of 2 to 6  
hydroxy  
groups per polyol molecule; alternatively, an average of 2.5 to 5  
hydroxy groups per polyol molecule; alternatively, an average of  
3 to 4  
hydroxy groups per polyol molecule; alternatively, an average of  
2.5 to  
3.5 hydroxy groups per polyol molecule; or alternatively, an  
average of  
2.5 to 4.5 hydroxy groups per polyol molecule.

DETD In yet another aspect, the polyol or mixture of polyols used to  
produce  
the \*\*\*thiol\*\*\* ester has a molecular weight or average  
molecular  
weight less than 500. In other embodiments, the polyol or mixture  
of  
polyols have a molecular weight or average molecular weight less  
than  
300; alternatively less than 200; alternatively, less than 150;  
or  
alternatively, less than 100.

DETD The \*\*\*thiol\*\*\* carboxylic acid and/or \*\*\*thiol\*\*\*  
carboxylic  
acid equivalent used to produce the \*\*\*thiol\*\*\* ester by  
contacting



a polyol and a \*\*\*thiol\*\*\* carboxylic acid and/or  
\*\*\*thiol\*\*\*  
carboxylic acid equivalent can be any \*\*\*thiol\*\*\* carboxylic  
acid  
mixture comprising \*\*\*thiol\*\*\* carboxylic acids,  
\*\*\*thiol\*\*\*  
carboxylic acid equivalent or mixture comprising \*\*\*thiol\*\*\*  
carboxylic acid equivalents that can produce the described  
\*\*\*thiol\*\*\*  
containing ester. When talking about the characteristics  
\*\*\*thiol\*\*\*  
carboxylic acid equivalent or \*\*\*thiol\*\*\* carboxylic acid  
equivalents, properties such as number of carbon atoms, average  
number  
of carbon atom, molecular weight or average molecular weight,  
number of  
\*\*\*thiol\*\*\* group, and average number of \*\*\*thiol\*\*\*  
groups, one  
will understand the these properties will apply to the portion of  
the  
\*\*\*thiol\*\*\* carboxylic acid equivalent which adds to the  
polyol to  
form the \*\*\*thiol\*\*\* ester.  
DETD In an aspect, the \*\*\*thiol\*\*\* carboxylic acid and/or  
\*\*\*thiol\*\*\*  
carboxylic acid equivalent used to produce the \*\*\*thiol\*\*\*  
ester  
comprises from 2 to 28 carbon atoms. In an embodiment, the  
\*\*\*thiol\*\*\*  
carboxylic acid and/or \*\*\*thiol\*\*\* carboxylic acid equivalent  
comprises from 4 to 26 carbon atoms; alternatively, from 8 to 24  
carbon  
atoms; alternatively, from 12 to 24 carbon atoms; or  
alternatively, from  
14 to 20 carbon atoms. In other embodiments, a mixture comprising  
\*\*\*thiol\*\*\* carboxylic acid and/or mixture comprising  
\*\*\*thiol\*\*\*  
carboxylic acid equivalents has an average of 2 to 28 carbon  
atoms per  
carboxylic acid and/or carboxylic acid equivalent; alternatively,  
from 4  
to 26 carbon atoms per carboxylic acid and/or carboxylic acid  
equivalent; alternatively, from 8 to 24 carbon atoms per  
carboxylic acid  
and/or carboxylic acid equivalent; alternatively, from 12 to 24  
carbon  
atoms per carboxylic acid and/or carboxylic acid equivalent; or  
alternatively, from 14 to 20 carbon atoms per carboxylic acid  
and/or  
carboxylic acid equivalent.  
DETD In another aspect, the \*\*\*thiol\*\*\* carboxylic acid and/or  
\*\*\*thiol\*\*\* carboxylic acid equivalent used to produce the  
\*\*\*thiol\*\*\* ester has at least 1 \*\*\*thiol\*\*\* group;  
alternatively  
2 \*\*\*thiol\*\*\* groups. In some embodiments, a mixture  
comprising  
\*\*\*thiol\*\*\* carboxylic acid and/or mixture comprising  
\*\*\*thiol\*\*\*  
carboxylic acid equivalents has an average of from 0.5 to 3  
\*\*\*thiol\*\*\* groups per carboxylic acid and/or carboxylic acid

equivalent; alternatively, an average of from 1 to 2  
 \*\*\*thiol\*\*\*  
 groups per carboxylic acid and/or carboxylic acid equivalent.  
 DETD In another aspect, the \*\*\*thiol\*\*\* carboxylic acid and/or  
 \*\*\*thiol\*\*\* carboxylic acid equivalent used to produce the  
 \*\*\*thiol\*\*\* ester has a molecular weight greater than 100;  
 alternatively greater than 180; alternatively greater than 240;  
 or  
 alternatively greater than 260. In other embodiments, the  
 \*\*\*thiol\*\*\*  
 carboxylic acid and/or \*\*\*thiol\*\*\* carboxylic acid equivalent  
 has a  
 molecular weight from 100 to 500; alternatively, from 120 to 420;  
 alternatively, from 180 to 420; alternatively, from 240 to 420; a  
 mixture or alternatively, from 260 to 360. In some embodiments, a  
 mixture comprising \*\*\*thiol\*\*\* carboxylic acid and/or mixture  
 comprising \*\*\*thiol\*\*\* carboxylic acid equivalents has an  
 average  
 molecular weight greater than 100 per carboxylic acid and/or  
 carboxylic  
 acid equivalent; alternatively greater than 180 per carboxylic  
 acid  
 and/or carboxylic acid equivalent; alternatively greater than 240  
 per  
 carboxylic acid and/or carboxylic acid equivalent; or  
 alternatively  
 greater than 260 per carboxylic acid and/or carboxylic acid  
 equivalent.  
 In yet other embodiments, the mixture comprising of \*\*\*thiol\*\*\*  
 carboxylic acid and/or mixture comprising \*\*\*thiol\*\*\*  
 carboxylic  
 acid equivalents has an average molecular weight from 100 to 500  
 per  
 carboxylic acid and/or carboxylic acid equivalent; alternatively,  
 from  
 120 to 420 per carboxylic acid and/or carboxylic acid equivalent;  
 alternatively, from 180 to 420 per carboxylic acid and/or  
 carboxylic  
 acid equivalent; alternatively, from 240 to 420 per carboxylic  
 acid  
 and/or carboxylic acid equivalent; a mixture or alternatively,  
 from 260  
 to 360 per carboxylic acid and/or carboxylic acid equivalent.  
 DETD In some aspects, the reaction between the polyol and the  
 \*\*\*thiol\*\*\*  
 containing carboxylic acid and/or \*\*\*thiol\*\*\* containing  
 carboxylic  
 acid derivative occurs in the presence of a solvent. In other  
 aspects  
 the reaction between the polyol and the \*\*\*thiol\*\*\*  
 containing  
 carboxylic acid and/or \*\*\*thiol\*\*\* containing carboxylic acid  
 derivative occurs in the substantial absence of a solvent. In  
 aspects  
 wherein the reaction between the polyol and the \*\*\*thiol\*\*\*  
 containing carboxylic acid and/or \*\*\*thiol\*\*\* containing  
 carboxylic  
 acid derivative occurs in the presence of a solvent, the solvent  
 is  
 selected from the group consisting of an aliphatic hydrocarbon,

an ether, an aromatic compound, or any combination thereof.  
Generally, the solvent, regardless of its chemical class, can include from 1 to 20 carbon atoms; or alternatively, from 3 to 10 carbon atoms. When the solvent includes the aliphatic hydrocarbon, the aliphatic hydrocarbon is butane, isobutane, pentane, hexane, heptane, octane, or any mixture thereof. When the solvent includes the aromatic compound, the aromatic compound is benzene, toluene, xylene, ethylbenzene, or any mixture thereof. When the solvent includes the ether, the ether is diethyl ether, dipropyl ether, tetrahydrofuran, and any mixture thereof.

DETD When a solvent is used for the reaction between the polyol and the \*\*\*thiol\*\*\* containing carboxylic acid and/or \*\*\*thiol\*\*\* containing carboxylic acid derivative, the quantity of solvent can be any amount that facilitates the reaction. In some embodiments, the mass of the solvent is less than 30 times the mass of the \*\*\*thiol\*\*\* containing carboxylic acid and/or \*\*\*thiol\*\*\* containing carboxylic acid derivative. In other embodiments, the mass of the solvent is less than 20 times the mass of the unsaturated ester oil; alternatively, less than 15 times the mass of the \*\*\*thiol\*\*\* containing carboxylic acid and/or \*\*\*thiol\*\*\* containing carboxylic acid derivative; alternatively, less than 10 times the mass of the \*\*\*thiol\*\*\* containing carboxylic acid and/or \*\*\*thiol\*\*\* containing carboxylic acid derivative; or alternatively, less than 5 times the mass of the \*\*\*thiol\*\*\* containing carboxylic acid and/or \*\*\*thiol\*\*\* containing carboxylic acid derivative. In other embodiments, the mass of the solvent is from 2 times to 20 times the mass of the \*\*\*thiol\*\*\* containing carboxylic acid and/or \*\*\*thiol\*\*\* containing carboxylic acid derivative; alternatively, from 3 times to 15 times the mass of the \*\*\*thiol\*\*\* containing carboxylic acid and/or \*\*\*thiol\*\*\* containing carboxylic acid derivative; or alternatively, from 5 times to 10 times the mass of the \*\*\*thiol\*\*\* containing carboxylic acid and/or \*\*\*thiol\*\*\* containing carboxylic acid derivative.

DETD The equivalent of \*\*\*thiol\*\*\* containing carboxylic acid and/or \*\*\*thiol\*\*\* containing carboxylic acid derivative carboxylic acid

groups to equivalents of polyol hydroxy groups molar ratio (hereinafter "carboxylic acid group to polyol hydroxy group molar ratio") utilized in the process to produce the \*\*\*thiol\*\*\* ester composition can be any carboxylic acid group to polyol hydroxy group molar ratio that produces the desired \*\*\*thiol\*\*\* ester composition. In some embodiments, the carboxylic acid group to polyol hydroxy group molar ratio is greater than 0.4. In other embodiments, the carboxylic acid group to polyol hydroxy group molar ratio is greater than 0.6; alternatively, greater than 0.8; alternatively, greater than 1; or alternatively, greater than 1.1. In other embodiments, the carboxylic acid group to polyol hydroxy group molar ratio can range from 0.4 to 1.3; alternatively, from 0.6 to 1.2, or alternatively, from 0.8 to 1.1.

DETD In some aspects, the reaction between the polyol and the \*\*\*thiol\*\*\* containing carboxylic acid and/or \*\*\*thiol\*\*\* containing carboxylic acid derivative is catalyzed. In some embodiments, the catalyst is a mineral acid, such as sulfuric or phosphoric acid. In other embodiments, the catalyst is an organic acid. In embodiments, for example, the organic acid is methane sulfonic acid or toluene sulfonic acid.

Other suitable types of catalyst will be apparent to those of skill in the art and are to be considered within the scope of the present invention.

DETD The reaction of the polyol and the \*\*\*thiol\*\*\* containing carboxylic acid and/or \*\*\*thiol\*\*\* containing carboxylic acid derivative can occur in a batch reactor or a continuous reactor, as described herein. The reaction between the polyol and the \*\*\*thiol\*\*\* containing carboxylic acid and/or \*\*\*thiol\*\*\* containing carboxylic acid derivative can be performed at any temperature capable of forming the \*\*\*thiol\*\*\* ester. In some embodiments, the polyol and the \*\*\*thiol\*\*\* containing carboxylic acid and/or \*\*\*thiol\*\*\* containing carboxylic acid derivative can be reacted at a temperature greater than 20.degree. C. In other embodiments, the polyol and the \*\*\*thiol\*\*\* containing carboxylic acid and/or \*\*\*thiol\*\*\* containing carboxylic acid derivative can be reacted at a temperature greater than 50.degree. C.; alternatively, greater than 75.degree. C.;

or alternatively, greater than 100.degree. C. In yet other embodiments, the polyol and the \*\*\*thiol\*\*\* containing carboxylic acid and/or \*\*\*thiol\*\*\* containing carboxylic acid derivative can be reacted at a temperature from 20.degree. C. to 250.degree. C.; alternatively, from 50.degree. C. to 200.degree. C.; alternatively, from 75.degree. C. to 175.degree. C.; or alternatively, from 100.degree. C. to 150.degree. C.

DETD The time required for the reaction of the polyol and the \*\*\*thiol\*\*\* containing carboxylic acid and/or \*\*\*thiol\*\*\* containing carboxylic acid derivative can be any time required to form the described \*\*\*thiol\*\*\* ester oil. Generally, the reaction time of the polyol and the \*\*\*thiol\*\*\* containing carboxylic acid and/or \*\*\*thiol\*\*\* containing carboxylic acid derivative is at least 5 minutes. In some embodiments, the reaction time is at least 30 minutes; alternatively, at least 1 hour; or alternatively, at least 2 hours. In yet other embodiments, the reaction time ranges from 5 minutes to 72 hours; alternatively, from 30 minutes to 48 hours; alternatively, from 1 hour minutes to 36 hours; or alternatively, from 2 hours and 24 hours.

DETD When a continuous reactor is used, a feed polyol weight unsaturated ester weight hourly space velocity ranging from 0.1 to 5 can be used to produce the desired \*\*\*thiol\*\*\* ester. Alternatively, the feed polyol weight hourly space velocity ranges between 0.1 to 5; alternatively, from 0.1 to 2. Alternatively, the feed polyol ester weight hourly space velocity is 0.1; alternatively, the feed polyol weight hourly space velocity is 0.25; or alternatively, the feed polyol weight hourly space velocity is 2.

DETD The reaction between the polyol and the \*\*\*thiol\*\*\* containing carboxylic acid and/or \*\*\*thiol\*\*\* containing carboxylic acid derivative can be performed at any reaction pressure that maintains the polyol and the \*\*\*thiol\*\*\* containing carboxylic acid and/or \*\*\*thiol\*\*\* containing carboxylic acid derivative in a liquid state. In some embodiments, the reaction between the polyol and the \*\*\*thiol\*\*\* containing carboxylic acid and/or \*\*\*thiol\*\*\* containing carboxylic acid derivative is performed at a pressure ranging from 0 psia to 2000 psia. In other embodiments, the reaction pressure ranges from 0 psia to 1000 psia; alternatively, from 0 psia and 500

psia; or alternatively, 0 psia to 300 psia.

DETD In some embodiments, the process to produce the \*\*\*thiol\*\*\* ester by reacting a polyol and the \*\*\*thiol\*\*\* containing carboxylic acid and/or \*\*\*thiol\*\*\* containing carboxylic acid derivative can further include a step to remove excess or residual polyol, \*\*\*thiol\*\*\* containing carboxylic acid, and/or \*\*\*thiol\*\*\* containing carboxylic acid derivative once the polyol has reacted with the \*\*\*thiol\*\*\* containing carboxylic acid or \*\*\*thiol\*\*\* containing carboxylic acid derivative. In some embodiments, the \*\*\*thiol\*\*\* ester is vacuum stripped. In some embodiments, the \*\*\*thiol\*\*\* ester is vacuum stripped at a temperature ranging between 25.degree. C. and 250.degree. C.; or alternatively, between 50.degree. C. and 200.degree. C. In other embodiments, the \*\*\*thiol\*\*\* ester is sparged with an inert gas to remove excess polyol, \*\*\*thiol\*\*\* containing carboxylic acid, and/or \*\*\*thiol\*\*\* containing carboxylic acid derivative. In some embodiments, the \*\*\*thiol\*\*\* ester is sparged with an inert gas at a temperature between 25.degree. C. and 250.degree. C.; or alternatively, between 50.degree. C. and 200.degree. C. In some aspects, the inert gas is nitrogen. Generally, the stripped or sparged \*\*\*thiol\*\*\* ester comprises less than 5 excess polyol, \*\*\*thiol\*\*\* containing carboxylic acid, or \*\*\*thiol\*\*\* containing carboxylic acid derivative. In other embodiments, the stripped or sparged \*\*\*thiol\*\*\* ester comprises less than 2 weight percent excess polyol, \*\*\*thiol\*\*\* containing carboxylic acid, and/or \*\*\*thiol\*\*\* containing carboxylic acid derivative; alternatively, less than 1 weight percent excess polyol, \*\*\*thiol\*\*\* containing carboxylic acid, and/or \*\*\*thiol\*\*\* containing carboxylic acid derivative; or alternatively, less than 0.5 weight percent excess polyol, \*\*\*thiol\*\*\* containing carboxylic acid, and/or \*\*\*thiol\*\*\* containing carboxylic acid derivative.

DETD Process for Making Hydroxy \*\*\*Thiol\*\*\* Ester Composition

DETD The present invention advantageously provides processes for producing a hydroxy \*\*\*thiol\*\*\* ester as embodiments of the present invention.

As an embodiment, the present invention includes a process to produce the hydroxy \*\*\*thiol\*\*\* ester. The process comprises the

steps of contacting hydrogen sulfide and an epoxidized unsaturated ester composition and reacting the hydrogen sulfide and the epoxidized unsaturated ester to form the hydroxy \*\*\*thiol\*\*\* ester. As another embodiment of the present invention, another process to produce the hydroxy \*\*\*thiol\*\*\* ester is provided. In this embodiment, the process comprises the steps of contacting a composition comprising a polyol with a composition comprising an hydroxy \*\*\*thiol\*\*\* containing carboxylic acid or an hydroxy \*\*\*thiol\*\*\* containing carboxylic acid derivative and reacting the polyol and the hydroxy \*\*\*thiol\*\*\* containing carboxylic acid or the hydroxy \*\*\*thiol\*\*\* containing carboxylic acid derivative to form the hydroxy \*\*\*thiol\*\*\* ester.

DETD Hydroxy \*\*\*Thiol\*\*\* Ester from Hydrogen Sulfide and an Epoxidized Unsaturated Ester Composition

DETD As an embodiment of the present invention, the hydroxy \*\*\*thiol\*\*\* ester composition is produced by a process comprising the steps of contacting hydrogen sulfide and an epoxidized unsaturated ester composition and reacting the hydrogen sulfide and the epoxidized unsaturated ester to produce the hydroxy \*\*\*thiol\*\*\* ester composition.

DETD In some embodiments, the epoxidized unsaturated ester composition includes epoxidized unsaturated esters that have an average of at least 1 ester groups and an average of at least 1 \*\*\*epoxide\*\*\* groups per epoxidized unsaturated ester molecule.

DETD The process for producing or preparing the hydroxy \*\*\*thiol\*\*\* ester composition can be applied to any of the epoxidized unsaturated esters described herein and used to produce any hydroxy \*\*\*thiol\*\*\* ester described herein. The process for producing the hydroxy \*\*\*thiol\*\*\* ester can also include any additional process steps or process conditions as described herein. Additionally, the process for producing the hydroxy \*\*\*thiol\*\*\* ester can form any hydroxy \*\*\*thiol\*\*\* ester described herein.

DETD In some aspects, the hydroxy \*\*\*thiol\*\*\* ester is produced by contacting hydrogen sulfide with the epoxidized natural source oil under the reaction conditions to form the hydroxy \*\*\*thiol\*\*\* ester in the presence of an optional catalyst. In some embodiments, the catalyst can be a heterogeneous catalyst or a homogeneous catalyst. Examples of

suitable catalysts are described herein. Additional types of suitable catalysts will be apparent to those of skill in the art and are to be considered within the scope of the present invention.

DETD The hydrogen sulfide to molar equivalents of \*\*\*epoxide\*\*\* groups in the epoxidized unsaturated ester (hereinafter "hydrogen sulfide to \*\*\*epoxide\*\*\* group molar ratio") utilized in the process to produce the hydroxy \*\*\*thiol\*\*\* ester can be any hydrogen sulfide to \*\*\*epoxide\*\*\* group molar ratio that produces the desired hydroxy \*\*\*thiol\*\*\* ester. The molar equivalents of epoxidized unsaturated ester epoxidized groups can be calculated by the equation:  
##EQU2##

In this equation, EUES GMW is the average gram molecular weight of the epoxidized unsaturated ester, EUES Mass is the mass of the epoxidized unsaturated ester, and EUES \*\*\*Epoxide\*\*\* is the average number of \*\*\*epoxide\*\*\* groups per epoxidized unsaturated ester molecule. In some embodiments, the hydrogen sulfide to \*\*\*epoxide\*\*\* group molar ratio is greater than 0.2. In other embodiments, the hydrogen sulfide to \*\*\*epoxide\*\*\* group molar ratio is greater than 0.5; alternatively, greater than 1; or alternatively, greater than 2. In other embodiments, the hydrogen sulfide to \*\*\*epoxide\*\*\* group molar ratio ranges from 0.2 to 5; alternatively, from 0.5 to 4; or alternatively, from 0.75 to 3. In some embodiments, the hydrogen sulfide to \*\*\*epoxide\*\*\* group molar ratio is greater than 2. In other embodiments, the hydrogen sulfide to \*\*\*epoxide\*\*\* group molar ratio is greater than 5; alternatively, greater than 10; alternatively, greater than 15; or alternatively, greater than 20. In other embodiments, the hydrogen sulfide to \*\*\*epoxide\*\*\* group molar ratio can be from 0.2 to 500; alternatively, from 0.5 to 400; alternatively, from 1 to 300; alternatively, from 2 to 250; alternatively, 5 to 200; or alternatively, from 10 to 100.

DETD The time required for the reaction of the epoxidized unsaturated ester and hydrogen sulfide can be any time required to form the described hydroxy \*\*\*thiol\*\*\* ester. Generally, the time required for the reaction of the epoxidized unsaturated ester and hydrogen sulfide is at



least 15 minutes. In some embodiments, the time required for the reaction of the unsaturated ester and hydrogen sulfide ranges from 15 minutes to 72 hours; alternatively, from 30 minutes to 48 hours; alternatively, from 45 minutes to 36 hours.

DETD In some embodiments, the hydroxy \*\*\*thiol\*\*\* ester composition includes hydroxy \*\*\*thiol\*\*\* ester molecules that have an average of greater than 2.5 weight percent \*\*\*thiol\*\*\* sulfur. In some embodiments, the hydroxy \*\*\*thiol\*\*\* ester composition includes hydroxy \*\*\*thiol\*\*\* ester molecules that have an average of greater than 5 weight percent \*\*\*thiol\*\*\* sulfur. Alternatively, in some embodiments, the hydroxy \*\*\*thiol\*\*\* ester molecules have an average ranging from 8 to 10 weight percent \*\*\*thiol\*\*\* sulfur.

DETD In other aspects, the process producing the hydroxy \*\*\*thiol\*\*\* ester composition includes producing hydroxy \*\*\*thiol\*\*\* ester molecules having an average of greater than 40 percent of the sulfide-containing ester total side chains comprise a sulfide group. Additional embodiments wherein the hydroxy \*\*\*thiol\*\*\* ester comprises a percentage of sulfide-containing ester total side chains are described herein.

DETD In embodiments, the process to produce the hydroxy \*\*\*thiol\*\*\* ester further comprises a step to remove residual hydrogen sulfide after reacting the hydrogen sulfide and the epoxidized unsaturated ester composition. In some embodiments, the hydroxy \*\*\*thiol\*\*\* ester is vacuum stripped. In some embodiments, the hydroxy \*\*\*thiol\*\*\* ester is vacuum stripped at a temperature ranging between 25.degree. C. and 250.degree. C.; or alternatively, between 50.degree. C. and 200.degree. C. In other embodiments, the hydroxy \*\*\*thiol\*\*\* ester is sparged with an inert gas to remove hydrogen sulfide. In some embodiments, the hydroxy \*\*\*thiol\*\*\* ester is sparged with an inert gas at a temperature between 25.degree. C. and 250.degree. C.; or alternatively, between 50.degree. C. and 200.degree. C. In some aspects, the inert gas is nitrogen. Generally, the stripped or sparged hydroxy \*\*\*thiol\*\*\* ester comprises less than 0.1 weight percent hydrogen sulfide. In other embodiments, the stripped or sparged hydroxy \*\*\*thiol\*\*\* ester comprises less than 0.05 weight percent hydrogen sulfide; alternatively,

less than 0.025 weight percent hydrogen sulfide; or alternatively, less than 0.01 weight percent hydrogen sulfide.

DETD The reaction between the hydrogen sulfide and the epoxidized unsaturated ester can be performed at any temperature capable of forming the hydroxy \*\*\*thiol\*\*\* ester. In some embodiments, the epoxidized unsaturated ester and hydrogen sulfide can be reacted at a reaction temperature greater than -20.degree. C. In other embodiments, the reaction temperature is greater than 0.degree. C.; alternatively, greater than 20.degree. C.; alternatively, greater than 50.degree. C.; or alternatively, greater than 80.degree. C. In yet other embodiments, the reaction temperature ranges from -20.degree. C. to 200.degree. C.; alternatively, from 20.degree. C. to 170.degree. C.; or alternatively, from 80.degree. C. to 140.degree. C.

DETD In another aspect, the process to produce a hydroxy \*\*\*thiol\*\*\* ester produces a hydroxy \*\*\*thiol\*\*\* ester having an \*\*\*epoxide\*\*\* group to \*\*\*thiol\*\*\* group molar ratio less than 3.3. In another aspect, the process to produce a hydroxy \*\*\*thiol\*\*\* ester produces a hydroxy \*\*\*thiol\*\*\* ester having an \*\*\*epoxide\*\*\* group to \*\*\*thiol\*\*\* group molar ratio less than 2. Other hydroxy \*\*\*thiol\*\*\* ester \*\*\*epoxide\*\*\* group to \*\*\*thiol\*\*\* group molar ratios are described herein. Alternatively, the hydroxy \*\*\*thiol\*\*\* ester \*\*\*epoxide\*\*\* group to \*\*\*thiol\*\*\* group molar ratio can be less than 1.5; alternatively, less than 1.0; alternatively, less than 0.5; alternatively, less than 0.25; or alternatively, less than 0.1. In other embodiments, the hydroxy \*\*\*thiol\*\*\* ester can be substantially free of \*\*\*epoxide\*\*\* groups.

DETD In another aspect, the process to produce hydroxy \*\*\*thiol\*\*\* ester produces a hydroxy \*\*\*thiol\*\*\* ester wherein at least 20 percent of the side chains comprise an .alpha.-hydroxy \*\*\*thiol\*\*\* group. Other hydroxy \*\*\*thiol\*\*\* ester embodiments wherein the hydroxy \*\*\*thiol\*\*\* ester contains a percentage of side chains comprising .alpha.-hydroxy \*\*\*thiol\*\*\* groups are described herein.

DETD Hydroxy \*\*\*Thiol\*\*\* Ester from a Polyol and a Hydroxy \*\*\*Thiol\*\*\* Containing Carboxylic Acid Derivative

DETD As another embodiment of the present invention, another process

to

prepare the hydroxy \*\*\*thiol\*\*\* ester is advantageously provided. In

this embodiment, the process includes the steps of contacting a composition comprising a polyol with a composition comprising a hydroxy

\*\*\*thiol\*\*\* containing carboxylic acid and/or \*\*\*thiol\*\*\* containing carboxylic acid derivative and reacting the polyol and hydroxy \*\*\*thiol\*\*\* containing carboxylic acid and/or hydroxy \*\*\*thiol\*\*\* containing carboxylic acid to form a hydroxy

\*\*\*thiol\*\*\* ester composition. This process can be applied to any polyol, any hydroxy \*\*\*thiol\*\*\* containing carboxylic acid, or any

\*\*\*thiol\*\*\* containing carboxylic acid derivative described herein. The process for

producing the hydroxy \*\*\*thiol\*\*\* ester composition can also include

any additional process steps or process conditions described herein.

Additionally, the process for producing the hydroxy \*\*\*thiol\*\*\* ester composition can form any \*\*\*thiol\*\*\* ester described herein.

DETD In some embodiments, the hydroxy \*\*\*thiol\*\*\* ester composition

includes hydroxy \*\*\*thiol\*\*\* ester molecules that have an average of

at least 1 ester groups per hydroxy \*\*\*thiol\*\*\* ester molecule and

an average of at least 1 .alpha.-hydroxy \*\*\*thiol\*\*\* groups per

hydroxy \*\*\*thiol\*\*\* ester molecule.

DETD The polyol used to produce the hydroxy \*\*\*thiol\*\*\* ester by contacting a polyol and a hydroxy \*\*\*thiol\*\*\* carboxylic acid and/or

hydroxy \*\*\*thiol\*\*\* carboxylic acid equivalent (for example a hydroxy \*\*\*thiol\*\*\* carboxylic acid methyl ester) can be any

polyol or mixture of polyols that can produce the described

\*\*\*thiol\*\*\* containing ester.

DETD In one aspect, the polyol used to produce the hydroxy \*\*\*thiol\*\*\*

ester can comprise from 2 to 20 carbon atoms. In other embodiments, the

polyol comprises from 2 to 10 carbon atoms; alternatively from 2 to 7

carbon atoms; alternatively from 2 to 5 carbon atoms. In further embodiments, the polyol may be a mixture of polyols having an

average of 2 to 20 carbon atoms; alternatively, an average of from 2 to 10

carbon atoms; alternatively, an average of 2 to 7 carbon atoms; alternatively

an average of 2 to 5 carbon atoms.

DETD In another aspect, the polyol used to produce the hydroxy \*\*\*thiol\*\*\*

ester can have any number of hydroxy groups needed to produce the hydroxy \*\*\*thiol\*\*\* ester as described herein. In some

embodiments,

the polyol has 2 hydroxy groups; alternatively 3 hydroxy groups; alternatively, 4 hydroxy groups; alternatively, 5 hydroxy groups;

or alternatively, 6 hydroxy groups. In other embodiments, the polyol comprises at least 2 hydroxy groups; alternatively at least 3 hydroxy groups; alternatively, at least 4 hydroxy groups; or alternatively, at least 5 hydroxy groups; at least 6 hydroxy groups. In yet other embodiments, the polyol comprises from 2 to 8 hydroxy groups; alternatively, from 2 to 4 hydroxy groups; or alternatively from 4 to 8 hydroxy groups.

DETD In further aspects, the polyol used to produce the hydroxy \*\*\*thiol\*\*\* ester is a mixture of polyols. In an embodiment, the mixture of polyols has an average of at least 1.5 hydroxy groups per polyol molecule. In other embodiments, the mixture of polyols has an average of at least 2 hydroxy groups per polyol molecule; alternatively, an average of at least 2.5 hydroxy groups per polyol molecule; alternatively, an average of at least 3.0 hydroxy groups per polyol molecule; or alternatively, an average of at least 4 hydroxy groups per polyol molecule. In yet another embodiment, the mixture of polyols has an average of 1.5 to 8 hydroxy groups per polyol molecule; alternatively, an average of 2 to 6 hydroxy groups per polyol molecule; alternatively, an average of 2.5 to 5 hydroxy groups per polyol molecule; alternatively, an average of 3 to 4 hydroxy groups per polyol molecule; alternatively, an average of 2.5 to 3.5 hydroxy groups per polyol molecule; or alternatively, an average of 2.5 to 4.5 hydroxy groups per polyol molecule.

DETD In yet another aspect, the polyol or mixture of polyols used to produce the hydroxy \*\*\*thiol\*\*\* ester has a molecular weight or average molecular weight less than 500. In other embodiments, the polyol or mixture of polyols have a molecular weight or average molecular weight less than 300; alternatively less than 200; alternatively, less than 150; or alternatively, less than 100.

DETD The hydroxy \*\*\*thiol\*\*\* carboxylic acid and/or hydroxy \*\*\*thiol\*\*\* carboxylic acid equivalent used to produce the hydroxy \*\*\*thiol\*\*\* ester by contacting a polyol and a hydroxy \*\*\*thiol\*\*\* carboxylic acid and/or hydroxy \*\*\*thiol\*\*\* carboxylic acid equivalent can be any hydroxy \*\*\*thiol\*\*\* carboxylic acid mixture comprising hydroxy \*\*\*thiol\*\*\* carboxylic acids, hydroxy

hydroxy      \*\*\*thiol\*\*\*      carboxylic acid equivalent or mixture comprising  
 described      \*\*\*thiol\*\*\*      carboxylic acid equivalents that can produce the  
 hydroxy      \*\*\*thiol\*\*\*      containing ester. When talking about the  
 characteristics hydroxy      \*\*\*thiol\*\*\*      carboxylic acid  
 equivalent or  
 hydroxy      \*\*\*thiol\*\*\*      carboxylic acid equivalents, properties  
 such as  
 number of carbon atoms, average number of carbon atom, molecular  
 weight  
 or average molecular weight, number of      \*\*\*thiol\*\*\*      group, and  
 average number of      \*\*\*thiol\*\*\*      groups, one will understand the  
 these  
 properties will apply to the portion of the      \*\*\*thiol\*\*\*  
 carboxylic  
 acid equivalent which adds to the polyol to form the  
 \*\*\*thiol\*\*\*  
 ester.  
 DETD      In an aspect, the hydroxy      \*\*\*thiol\*\*\*      carboxylic acid and/or  
 hydroxy      \*\*\*thiol\*\*\*      carboxylic acid equivalent used to  
 produce the  
         \*\*\*thiol\*\*\*      ester comprises from 2 to 28 carbon atoms. In an  
 embodiment, the hydroxy      \*\*\*thiol\*\*\*      carboxylic acid and/or  
 hydroxy  
         \*\*\*thiol\*\*\*      carboxylic acid equivalents comprises from 4 to  
 26 carbon  
 atoms; alternatively, from 8 to 24 carbon atoms; alternatively,  
 from 12  
 to 24 carbon atoms; or alternatively, from 14 to 20 carbon atoms.  
 In  
         other embodiments, a mixture comprising hydroxy      \*\*\*thiol\*\*\*  
         carboxylic acids and/or mixture comprising hydroxy      \*\*\*thiol\*\*\*  
         carboxylic acid equivalents has an average of 2 to 28 carbon  
 atoms per  
         carboxylic acid and/or carboxylic acid equivalent; alternatively,  
 from 4  
 to 26 carbon per carboxylic acid and/or carboxylic acid  
 equivalent;  
         alternatively, from 8 to 24 carbon atoms per carboxylic acid  
 and/or  
         carboxylic acid equivalent; alternatively, from 12 to 24 carbon  
 atoms  
         per carboxylic acid and/or carboxylic acid equivalent; or  
 alternatively,  
         from 14 to 20 carbon atoms per carboxylic acid and/or carboxylic  
 acid  
         equivalent.  
 DETD      In another aspect, the hydroxy      \*\*\*thiol\*\*\*      carboxylic acid  
 and/or  
         hydroxy      \*\*\*thiol\*\*\*      carboxylic acid equivalent used to  
 produce the  
         \*\*\*thiol\*\*\*      ester has at least 1      \*\*\*thiol\*\*\*      group;  
 alternatively  
         2      \*\*\*thiol\*\*\*      groups. In some embodiments, a mixture  
 comprising  
         hydroxy      \*\*\*thiol\*\*\*      carboxylic acids and/or mixture  
 comprising  
         hydroxy      \*\*\*thiol\*\*\*      carboxylic acid equivalents has an  
 average of

from 0.5 to 3 \*\*\*thiol\*\*\* groups per carboxylic acid and/or carboxylic acid equivalent; alternatively, an average of from 1 to 2 \*\*\*thiol\*\*\* groups per carboxylic acid and/or carboxylic acid equivalent.

DETD In another aspect, the hydroxy \*\*\*thiol\*\*\* carboxylic acid and/or hydroxy \*\*\*thiol\*\*\* carboxylic acid equivalent used to produce the \*\*\*thiol\*\*\* ester has at least 1 hydroxy group; alternatively, at least 2 hydroxy groups. In some embodiments, a mixture comprising hydroxy \*\*\*thiol\*\*\* carboxylic acids and/or mixture comprising hydroxy \*\*\*thiol\*\*\* carboxylic acid equivalents has an average of from 0.5 to 3 hydroxy groups per carboxylic acid and/or carboxylic acid equivalent; alternatively, an average of from 1 to 2 hydroxy groups per carboxylic acid and/or carboxylic acid equivalent.

DETD In another aspect, the hydroxy \*\*\*thiol\*\*\* carboxylic acid and/or hydroxy \*\*\*thiol\*\*\* carboxylic acid equivalent used to produce the hydroxy \*\*\*thiol\*\*\* ester has a molecular weight greater than 100; alternatively greater than 180; alternatively greater than 240; or alternatively greater than 260. In other embodiments, the hydroxy \*\*\*thiol\*\*\* carboxylic acid and/or hydroxy \*\*\*thiol\*\*\* carboxylic acid equivalent has a molecular weight from 100 to 500; alternatively, from 120 to 420; alternatively, from 180 to 420; alternatively, from 240 to 420; a mixture or alternatively, from 260 to 360. In some embodiments, a mixture comprising hydroxy \*\*\*thiol\*\*\* carboxylic acids and/or mixture comprising hydroxy \*\*\*thiol\*\*\* carboxylic acid equivalents has an average molecular weight greater than 100 per carboxylic acid and/or carboxylic acid equivalent; alternatively greater than 180 per carboxylic acid and/or carboxylic acid equivalent; alternatively greater than 240 per carboxylic acid and/or carboxylic acid equivalent; or alternatively greater than 260 per carboxylic acid and/or carboxylic acid equivalent. In yet other embodiments, the mixture comprising hydroxy \*\*\*thiol\*\*\* carboxylic acid and/or mixture comprising hydroxy \*\*\*thiol\*\*\* carboxylic acid equivalents has an average molecular weight from 100 to 500 per carboxylic acid and/or carboxylic acid equivalent; alternatively, from 120 to 420 per carboxylic acid and/or carboxylic acid equivalent; alternatively, from 180 to 420 per carboxylic acid and/or carboxylic acid equivalent;

alternatively, from 240 to 420 per carboxylic acid and/or carboxylic acid equivalent; a mixture or alternatively, from 260 to 360 per carboxylic acid and/or carboxylic acid equivalent.

DETD In some aspects, the reaction between the polyol and the hydroxy \*\*\*thiol\*\*\* containing carboxylic acid and/or hydroxy \*\*\*thiol\*\*\* containing carboxylic acid derivative occurs in the presence of a solvent. In other aspects, the reaction between the polyol and the hydroxy \*\*\*thiol\*\*\* containing carboxylic acid and/or hydroxy \*\*\*thiol\*\*\* containing carboxylic acid derivative occurs in the substantial absence of a solvent. In aspects wherein the reaction between the polyol and the hydroxy \*\*\*thiol\*\*\* containing carboxylic acid and/or hydroxy \*\*\*thiol\*\*\* containing carboxylic acid derivative occurs in the presence of a solvent, the solvent is selected from the group consisting of an aliphatic hydrocarbon, an ether, an aromatic compound, or any combination thereof. Generally, the solvent, regardless of its chemical class, includes from 1 to 20 carbon atoms; alternatively, from 3 to 10 carbon atoms. When the solvent includes the aliphatic hydrocarbon, the aliphatic hydrocarbon is butane, isobutane, pentane, hexane, heptane, octane, or any mixture thereof. When the solvent includes the aromatic compound, the aromatic compound is benzene, toluene, xylene, ethylbenzene, or any mixture thereof.

When the solvent includes the ether, the ether is diethyl ether, dipropyl ether, tetrahydrofuran, and any mixture thereof.

DETD When a solvent is used for the reaction between the polyol and the hydroxy \*\*\*thiol\*\*\* containing carboxylic acid and/or hydroxy \*\*\*thiol\*\*\* containing carboxylic acid derivative, the quantity of solvent can be any amount that facilitates the reaction. In some embodiments, the mass of the solvent is less than 30 times the mass of the hydroxy \*\*\*thiol\*\*\* containing carboxylic acid and/or hydroxy \*\*\*thiol\*\*\* containing carboxylic acid derivative. In other embodiments, the mass of the solvent is less than 20 times the mass of the hydroxy \*\*\*thiol\*\*\* ester; alternatively, less than 15 times the mass of the hydroxy \*\*\*thiol\*\*\* containing carboxylic acid and/or hydroxy \*\*\*thiol\*\*\* containing carboxylic acid derivative; alternatively, less than 10 times the mass of the hydroxy \*\*\*thiol\*\*\* containing carboxylic acid and/or hydroxy \*\*\*thiol\*\*\* containing carboxylic acid derivative; or alternatively, less than 5 times

the mass  
 of the hydroxy \*\*\*thiol\*\*\* containing carboxylic acid and/or  
 hydroxy  
 \*\*\*thiol\*\*\* containing carboxylic acid derivative. In other  
 embodiments, the mass of the solvent is from 2 times to 20 times  
 the  
 mass of the hydroxy \*\*\*thiol\*\*\* containing carboxylic acid  
 and/or  
 hydroxy \*\*\*thiol\*\*\* containing carboxylic acid derivative;  
 alternatively, from 3 times to 15 times the mass of the hydroxy  
 \*\*\*thiol\*\*\* containing carboxylic acid and/or hydroxy  
 \*\*\*thiol\*\*\*  
 containing carboxylic acid derivative; or alternatively, from 5  
 times to  
 10 times the mass of the hydroxy \*\*\*thiol\*\*\* containing  
 carboxylic  
 acid and/or hydroxy \*\*\*thiol\*\*\* containing carboxylic acid  
 derivative.  
 DETD The equivalents of hydroxy \*\*\*thiol\*\*\* containing carboxylic  
 acid  
 derivative and/or hydroxy \*\*\*thiol\*\*\* containing carboxylic  
 acid  
 derivative carboxylic acid groups to equivalents of polyol  
 hydroxy  
 groups molar ratio (hereinafter referred to as "carboxylic acid  
 group to  
 polyol hydroxy group molar ratio") utilized in the process to  
 produce  
 the hydroxy \*\*\*thiol\*\*\* ester can be any carboxylic acid  
 group to  
 polyol hydroxy group molar ratio that produces the desired  
 hydroxy  
 \*\*\*thiol\*\*\* ester. In some embodiments, the carboxylic acid  
 group to  
 polyol hydroxy group molar ratio is greater than 0.4. In other  
 embodiments, the carboxylic acid group to polyol hydroxy group  
 molar  
 ratio is greater than 0.6; alternatively, greater than 0.8;  
 alternatively, greater than 1; or alternatively, greater than  
 1.1. In  
 other embodiments, the carboxylic acid group to polyol hydroxy  
 group  
 molar ratio ranges from 0.4 to 1.3; alternatively, from 0.6 to  
 1.2, or  
 alternatively, from 0.8 to 1.1.  
 DETD In some aspects, the reaction between the polyol and the hydroxy  
 \*\*\*thiol\*\*\* containing carboxylic acid and/or hydroxy  
 \*\*\*thiol\*\*\*  
 containing carboxylic acid derivative is catalyzed. In some  
 embodiments,  
 the catalyst is a mineral acid, such as sulfuric or phosphoric  
 acid. In  
 other embodiments, the catalyst is an organic acid. In  
 embodiments, for  
 example, the organic acid is methane sulfonic acid or toluene  
 sulfonic  
 acid. Other suitable types of catalyst will be apparent to those  
 of  
 skill in the art and are to be considered within the scope of the  
 present invention.



DETD     The reaction of the polyol and the hydroxy     \*\*\*thiol\*\*\*  
containing  
          carboxylic acid and/or hydroxy     \*\*\*thiol\*\*\*     containing  
carboxylic  
          acid derivative can occur in a batch reactor or a continuous  
reactor, as  
          described herein. The reaction between the polyol and the hydroxy  
          \*\*\*thiol\*\*\*     containing carboxylic acid and/or hydroxy  
\*\*\*thiol\*\*\*  
          containing carboxylic acid derivative can be performed at any  
          temperature capable of forming the hydroxy     \*\*\*thiol\*\*\*     ester.

In  
          some embodiments, the polyol and the hydroxy     \*\*\*thiol\*\*\*  
containing  
          carboxylic acid and/or hydroxy     \*\*\*thiol\*\*\*     containing  
carboxylic  
          acid derivative can be reacted at a temperature greater than  
20.degree.  
          C. In other embodiments, the polyol and the hydroxy     \*\*\*thiol\*\*\*  
          containing carboxylic acid and/or hydroxy     \*\*\*thiol\*\*\*  
containing  
          carboxylic acid derivative can be reacted at a temperature  
greater than  
          50.degree. C.; alternatively, greater than 75.degree. C.; or  
          alternatively, greater than 100.degree. C. In yet other  
embodiments, the  
          polyol and the hydroxy     \*\*\*thiol\*\*\*     containing carboxylic acid  
and/or  
          hydroxy     \*\*\*thiol\*\*\*     containing carboxylic acid derivative can  
be  
          reacted at a temperature from 20.degree. C. to 250.degree. C.;  
          alternatively, from 50.degree. C. to 200.degree. C.;  
alternatively, from  
          75.degree. C. to 175.degree. C.; or alternatively, from  
100.degree. C.  
          to 150.degree..

DETD     The time required for the reaction of the polyol and the hydroxy  
          \*\*\*thiol\*\*\*     containing carboxylic acid and/or hydroxy  
\*\*\*thiol\*\*\*  
          containing carboxylic acid derivative can be any time required to  
form  
          the described hydroxy     \*\*\*thiol\*\*\*     ester composition.  
Generally, the  
          reaction time is at least 5 minutes. In some embodiments, the  
reaction  
          time is at least 30 minutes; alternatively, at least 1 hour; or  
          alternatively, at least 2 hours. In yet other embodiments, the  
reaction  
          time ranges from 5 minutes to 72 hours; alternatively, from 30  
minutes  
          to 48 hours; alternatively, from 1 hour minutes to 36 hours; or  
          alternatively, from 2 hours and 24 hours.

DETD     The reaction between the polyol and the hydroxy     \*\*\*thiol\*\*\*  
          containing carboxylic acid and/or hydroxy     \*\*\*thiol\*\*\*  
containing  
          carboxylic acid derivative can be performed at any reaction  
pressure  
          that maintains the polyol and the hydroxy     \*\*\*thiol\*\*\*  
containing  
          carboxylic acid and/or hydroxy     \*\*\*thiol\*\*\*     containing

carboxylic acid derivative in a liquid state. In some embodiments, the reaction pressure ranges from 0 psia to 2000 psia. In other embodiments, the reaction pressure ranges from 0 psia to 1000 psia; alternatively, from 0 psia and 500 psia; or alternatively, from 0 psia to 300 psia.

DETD In some embodiments, the process to produce the hydroxy \*\*\*thiol\*\*\* ester composition by reacting a polyol and the hydroxy \*\*\*thiol\*\*\* containing carboxylic acid and/or hydroxy \*\*\*thiol\*\*\* containing carboxylic acid derivative can further include a step to remove excess or residual polyol, hydroxy \*\*\*thiol\*\*\* containing carboxylic acid, and/or hydroxy \*\*\*thiol\*\*\* containing carboxylic acid derivative once the polyol has reacted with the hydroxy \*\*\*thiol\*\*\* containing carboxylic acid or hydroxy \*\*\*thiol\*\*\* containing carboxylic acid derivative. In some embodiments, the \*\*\*thiol\*\*\* ester is vacuum stripped. In some embodiments, the hydroxy \*\*\*thiol\*\*\* ester is vacuum stripped at a temperature between 25.degree. C. and 250.degree. C.; or alternatively, between 50.degree. C. and 200.degree. C. In other embodiments, the hydroxy \*\*\*thiol\*\*\* ester is sparged with an inert gas to remove excess polyol, hydroxy \*\*\*thiol\*\*\* containing carboxylic acid, and/or hydroxy \*\*\*thiol\*\*\* containing carboxylic acid derivative. In some embodiments, the hydroxy \*\*\*thiol\*\*\* ester is sparged with an inert gas at a temperature between 25.degree. C. and 250.degree. C., or alternatively, between 50.degree. C. and 200.degree. C. In some aspects, the inert gas is nitrogen. Generally, the stripped or sparged hydroxy \*\*\*thiol\*\*\* ester oil comprises less than 5 excess polyol, hydroxy \*\*\*thiol\*\*\* containing carboxylic acid, or hydroxy \*\*\*thiol\*\*\* containing carboxylic acid derivative. In other embodiments, the stripped or sparged hydroxy \*\*\*thiol\*\*\* ester oil comprises less than 2 weight percent excess polyol, hydroxy \*\*\*thiol\*\*\* containing carboxylic acid, and/or hydroxy \*\*\*thiol\*\*\* containing carboxylic acid derivative; less than 1 weight percent excess polyol, hydroxy \*\*\*thiol\*\*\* containing carboxylic acid, and/or

hydroxy \*\*\*thiol\*\*\* containing carboxylic acid derivative; or alternatively, less than 0.5 weight percent excess polyol,

hydroxy \*\*\*thiol\*\*\* containing carboxylic acid, and/or hydroxy \*\*\*thiol\*\*\* containing carboxylic acid derivative.

DETD A method of making a thioacrylate containing ester composition is advantageously provided as another embodiment of the present invention.

The process for producing the thioacrylate containing ester comprising contacting a \*\*\*thiol\*\*\* ester with an acrylate and converting at least one \*\*\*thiol\*\*\* group to a \*\*\*thiol\*\*\* acrylate group. The process can be applied to any of the \*\*\*thiol\*\*\* esters described herein and used to any thioacrylate ester described herein. The process for producing the thioacrylate ester can also include any additional process steps or process conditions described herein.

DETD The acrylate compound can be any acrylate compound capable of reacting with a \*\*\*thiol\*\*\* group to form the \*\*\*thiol\*\*\* acrylate group.

In some embodiments, the acrylate compound can be an acrylic halide. In other embodiments, the acrylate compound can be an acrylic acid. In yet other embodiments, the acrylate compound can be an acrylic anhydride.

DETD In some aspects, the conversion of the \*\*\*thiol\*\*\* group to a thioacrylate group occurs in the presence of a solvent. In other aspects the conversion of the \*\*\*thiol\*\*\* group to a thioacrylate group occurs in the substantial absence of a solvent. In aspects wherein the conversion of the \*\*\*thiol\*\*\* group to a thioacrylate group occurs in the presence of a solvent, the solvent may be an aliphatic hydrocarbon, an ether, and aromatic compound. Generally, the solvent, regardless of its chemical class, includes from 1 to 20 carbon atoms; or alternatively, from 3 to 10 carbon atoms. When the solvent includes the aliphatic hydrocarbon, the aliphatic hydrocarbon is butane, isobutane, pentane, hexane, heptane, octane, or any mixture thereof. When the solvent includes the aromatic compound, the aromatic compound is benzene, toluene, xylene, ethylbenzene, or any mixture thereof. When the solvent includes the ether, the ether is diethyl ether, dipropyl ether, tetrahydrofuran, or any mixture thereof.

DETD When a solvent is used for the conversion of the \*\*\*thiol\*\*\* group to a thioacrylate group, the quantity of solvent can be any amount that facilitates the reaction. In some embodiments, the mass of the solvent is less than 30 times the mass of the \*\*\*thiol\*\*\* ester. In other embodiments, the mass of the solvent is less than 20 times the mass of the \*\*\*thiol\*\*\* ester; alternatively, less than 15 times the mass of the \*\*\*thiol\*\*\* ester; alternatively, less than 10 times the mass of the \*\*\*thiol\*\*\* ester; or alternatively, less than 5 times the mass of the \*\*\*thiol\*\*\* ester. In other embodiments, the mass of the solvent is from 2 times to 20 times the mass of the \*\*\*thiol\*\*\* ester; alternatively, from 3 times to 15 times the mass of the \*\*\*thiol\*\*\* ester; alternatively, 4 times to 15 times the mass of the \*\*\*thiol\*\*\* ester; or alternatively, from 5 times to 10 times the mass of the \*\*\*thiol\*\*\* ester.

DETD In some aspects the conversion of the \*\*\*thiol\*\*\* group to the thioacrylate group occurs in the presence of a catalyst. In some embodiments, the catalyst is homogeneous. In some embodiments, the catalyst is an organic amine. Examples of suitable organic amines include triethylamine, tripropylamine, tributylamine, and pyridine. In other embodiments, the catalyst is heterogeneous. Examples of suitable catalysts include Amberlyst A-21 and Amberlyst A-26. Other suitable catalysts will be apparent to those of skill in the art and are to be considered within the scope of the present invention.

DETD The conversion of the \*\*\*thiol\*\*\* group to a thioacrylate group can be performed at any conversion temperature that is capable of converting the \*\*\*thiol\*\*\* group to a thioacrylate group. In some embodiments, the conversion temperature is greater than -20.degree. C. In other embodiments, the conversion temperature is greater than 0.degree. C.; alternatively, greater than 20.degree. C.; alternatively, greater than 50.degree. C.; alternatively, greater than 80.degree. C.; or alternatively, greater than 100.degree. C. In yet other embodiments, the conversion temperature ranges from -20.degree. C. to 250.degree. C.; alternatively, from 20.degree. C. to 200.degree. C.; or alternatively, from 50.degree. C. to 150.degree. C.

DETD The conversion time required for the conversion of the  
\*\*\*thiol\*\*\*  
group to a thioacrylate group can be any time required to form  
the  
described thioacrylate containing ester. Generally, the  
conversion time  
is at least 5 minutes. In some embodiments, the conversion time  
is at  
least 15 minutes; alternatively, at least 30 minutes;  
alternatively, at  
least 45 minutes; or alternatively, at least 1 hour. In other  
embodiments, the conversion time ranges from 15 minutes to 12  
hours;  
alternatively, from 30 minutes to 6 hours; or alternatively, from  
45  
minutes to 3 hours.

DETD The conversion of the \*\*\*thiol\*\*\* group to a thioacrylate  
group can  
be performed at any conversion pressure that maintains the  
\*\*\*thiol\*\*\*  
ester and the acrylate compound in the liquid state. In some  
embodiments, the conversion pressure ranges from 0 psia to 2000  
psia. In  
other embodiments, the conversion pressure ranges from 0 psia to  
1000  
psia; or alternatively, from 0 psia to 500 psia.

DETD Process for Producing Cross-Linked \*\*\*Thiol\*\*\* Ester

DETD As an embodiment of the present invention, a process for  
producing a  
cross-linked \*\*\*thiol\*\*\* ester composition is advantageously  
provided. Minimally, in some embodiments, the process to produce  
the  
cross-linked \*\*\*thiol\*\*\* ester composition comprises  
contacting a  
\*\*\*thiol\*\*\* ester composition with an oxidizing agent and  
reacting the  
\*\*\*thiol\*\*\* ester composition and an oxidizing agent to form  
the  
\*\*\*thiol\*\*\* ester oligomer having at least two \*\*\*thiol\*\*\*  
ester  
monomers connected by a polysulfide linkage having the structure  
--S.sub.Q-- , wherein Q is an integer greater than 1. The  
disclosed  
method may be applied to any \*\*\*thiol\*\*\* ester described  
herein to  
produce any cross-linked \*\*\*thiol\*\*\* ester composition as  
described  
herein. The process to produce the cross-linked \*\*\*thiol\*\*\*  
ester  
composition can also include any additional process steps or  
process  
conditions as described herein.

DETD When elemental sulfur is used as the oxidizing agent, the  
quantity of  
elemental sulfur utilized to form the cross-linked \*\*\*thiol\*\*\*  
ester  
composition is determined as a function of the \*\*\*thiol\*\*\*  
sulfur  
content of the \*\*\*thiol\*\*\* ester composition. In an aspect,  
the

weight ratio of elemental sulfur to \*\*\*thiol\*\*\* sulfur in the  
\*\*\*thiol\*\*\* ester composition is at least 0.5. In some  
embodiments,

the weight ratio of elemental sulfur to \*\*\*thiol\*\*\* sulfur in  
the

\*\*\*thiol\*\*\* ester composition is at least 5; alternatively,  
at least  
10, alternatively, at least 15, or alternatively, at least 20. In  
other

embodiments, the weight ratio of elemental sulfur to  
\*\*\*thiol\*\*\*

sulfur in the \*\*\*thiol\*\*\* ester composition ranges from 0.5  
to 32;

alternatively, ranges from 1 to 24; alternatively, ranges from 2  
to 16;

or alternatively, ranges from 3 to 10.

DETD In an aspect, the reaction of the \*\*\*thiol\*\*\* ester and  
elemental

sulfur occurs in the presence of a catalyst. The catalyst can be  
any

catalyst that catalyzes the formation of the polysulfide linkage  
between

at least two \*\*\*thiol\*\*\* ester monomers. In some embodiments,  
the

catalyst is an amine. In further embodiments, the catalyst is a  
tertiary

amine.

DETD The formation of the cross-linked \*\*\*thiol\*\*\* ester can  
occur in a

batch reactor or a continuous reactor, as described herein. The  
formation of the cross-linked \*\*\*thiol\*\*\* ester can occur at

any

temperature capable of forming the \*\*\*thiol\*\*\* ester. In some  
embodiments, the formation of the cross-linked \*\*\*thiol\*\*\*

ester can

occur at a temperature greater than 25.degree. C. In other  
embodiments,

the formation of the cross-linked \*\*\*thiol\*\*\* ester can  
occur at a

temperature greater than 50.degree. C.; alternatively, greater  
than

70.degree. C.; or alternatively, greater than 80.degree. C. In  
yet other

embodiments, the formation of the cross-linked \*\*\*thiol\*\*\*  
ester

occurs at a temperature from 25.degree. C. to 150.degree. C.;  
alternatively, from 50.degree. C. to 150.degree. C.;

alternatively, from

70.degree. C. to 120.degree. C.; or alternatively, from  
80.degree. C. to

110.degree. C.

DETD The time required to form the cross-linked \*\*\*thiol\*\*\* ester  
can be

any time required to form the desired cross-linked \*\*\*thiol\*\*\*  
ester. Generally, the time required to form the cross-linked

\*\*\*thiol\*\*\* ester is at least 15 minutes. In some  
embodiments, the

time required to form the cross-linked \*\*\*thiol\*\*\* ester is  
at least

30 minutes; alternatively, at least 1 hour; or alternatively, at

least 2  
hours. In yet other embodiments, the time required to form the  
cross-linked \*\*\*thiol\*\*\* ester ranges from 15 minutes to 72  
hours;  
alternatively, from 30 minutes to 48 hours; alternatively, from 1  
hour  
minutes to 36 hours; or alternatively, from 2 hours and 24 hours.  
DETD In embodiments, the process to produce the cross-linked  
\*\*\*thiol\*\*\*  
ester further comprises a step to remove residual hydrogen  
sulfide. In  
some embodiments the cross-linked \*\*\*thiol\*\*\* ester is vacuum  
stripped. In some embodiments, the cross-linked \*\*\*thiol\*\*\*  
ester is  
vacuum striped at a temperature between 25.degree. C. and  
250.degree.  
C.; alternatively, between 50.degree. C. and 200.degree. C.; or  
alternatively, 75 and 150.degree. C. In some embodiments, the  
cross-linked \*\*\*thiol\*\*\* ester oil is sparged with an inert  
gas to  
remove residual hydrogen sulfide. In other embodiments, the  
cross-linked  
\*\*\*thiol\*\*\* ester is sparged with an inert gas at a  
temperature  
between 25.degree. C. and 250.degree. C.; alternatively, between  
50.degree. C. and 200.degree. C.; or alternatively, between 75  
and  
150.degree. C. In yet other embodiments, the vacuum stripping is  
performed while sparging the cross-linked \*\*\*thiol\*\*\* ester  
with an  
inert gas. In yet other embodiments, the vacuum stripping is  
performed  
while sparging the cross-linked \*\*\*thiol\*\*\* ester an inert  
gas at a  
temperature between 25.degree. C. and 250.degree. C.;  
alternatively,  
between 50.degree. C. and 200.degree. C.; or alternatively, 75  
and  
150.degree. C. In some embodiments, the inert gas is nitrogen.  
DETD Generally, the stripped or sparged cross-linked \*\*\*thiol\*\*\*  
ester  
comprises less than 0.1 weight percent hydrogen sulfide. In other  
embodiments, the stripped or sparged \*\*\*thiol\*\*\* -containing  
ester  
oil comprises less than 0.05 weight percent hydrogen sulfide;  
alternatively, less than 0.025 weight percent hydrogen sulfide;  
or  
alternatively, less than 0.01 weight percent hydrogen sulfide.  
DETD The present invention advantageously provides processes for  
producing  
sulfide-containing esters as embodiments of the present  
invention.  
Generally, the sulfide-containing esters can be prepared by two  
processes. As an embodiment of the present invention, the first  
process  
used to produce a sulfide-containing ester comprises contacting  
an  
unsaturated ester and a \*\*\*mercaptan\*\*\* and reacting the  
unsaturated  
ester and \*\*\*mercaptan\*\*\* to form a sulfide-containing ester.

As

another embodiment of the present invention, the second process used to

produce a sulfide-containing ester comprises contacting an epoxidized

unsaturated ester and a \*\*\*mercaptan\*\*\* sulfide and reacting the

unsaturated ester and \*\*\*mercaptan\*\*\* to form a sulfide-containing

ester. Additional aspects of the two sulfide-containing ester production

processes are described below.

DETD The sulfide-containing esters and sulfide-containing ester compositions

described herein can be produced by a process comprising contacting a

\*\*\*mercaptan\*\*\* and an unsaturated ester and reacting the

\*\*\*mercaptan\*\*\* and the unsaturated ester to form a sulfide-containing

ester. The process can be applied to any of the unsaturated esters and

\*\*\*mercaptans\*\*\* described herein. The process for producing the

sulfide-containing ester can also include any additional process steps

or process conditions described herein. Additionally, the process for

producing the sulfide-containing ester can form any sulfide-containing

ester described herein.

DETD In some aspects, the reaction between the \*\*\*mercaptan\*\*\* and the

unsaturated ester occurs in the presence of a solvent. In other aspects

the reaction between the \*\*\*mercaptan\*\*\* and the unsaturated ester

occurs in the substantial absence of a solvent. When the reaction occurs

in the presence of a solvent, the solvent is selected from an aliphatic

hydrocarbon, an ether, an aromatic compound, an alcohol, or any combination thereof. Generally, the solvent, regardless of its chemical

class, can comprise from 1 to 20 carbon atoms; alternatively, from 3 to

10 carbon atoms. When the solvent includes an aliphatic hydrocarbon, the

aliphatic hydrocarbon is butane, isobutane, pentane, hexane, heptane,

octane, or any mixture thereof. When the solvent includes an aromatic

compound, the aromatic compound is benzene, toluene, xylene, ethylbenzene, or any mixture thereof. When the solvent includes

an alcohol, the alcohol is methanol, 1-propanol, 2-propanol, 1-butanol,

2-butanol, 2-methyl-2-propanol, or any mixture thereof. When the solvent

includes an ether, the ether is diethyl ether, dipropyl ether, tetrahydrofuran, or any mixture thereof.



DETD When a solvent is used for the reaction between the  
\*\*\*mercaptan\*\*\*  
and the unsaturated ester, the quantity of solvent can be any  
amount  
that facilitates the reaction, as understood by those of skill in  
the  
art. In some embodiments, the mass of the solvent is less than 30  
times  
the mass of the unsaturated ester. In other embodiments, the mass  
of the  
solvent is less than 20 times the mass of the unsaturated ester;  
alternatively, less than 15 times the mass of the unsaturated  
ester;  
alternatively, less than 10 times the mass of the unsaturated  
ester; or  
alternatively, less than 5 times the mass of the unsaturated  
ester. In  
other embodiments, the mass of the solvent is from 2 times to 20  
times  
the mass of the unsaturated ester; alternatively, from 3 times to  
15  
times the mass of the unsaturated ester; alternatively, from 4  
times to  
15 times the mass of the unsaturated ester; or alternatively,  
from 5  
times to 10 times the mass of the unsaturated ester.

DETD The molar ratio of \*\*\*mercaptan\*\*\* to molar equivalents of  
unsaturated ester carbon-carbon double bonds (herein after "  
\*\*\*mercaptan\*\*\* to carbon-carbon double bond molar ratio")  
utilized in  
the process to produce the sulfide-containing ester can be any  
\*\*\*mercaptan\*\*\* to carbon-carbon double bond molar ratio that  
produces  
the desired sulfide-containing ester. The molar equivalents of  
unsaturated ester carbon-carbon double bonds is calculated by the  
equation:  $\frac{\text{UES C.dbd.C}}{\text{UES GMW}}$  In this equation, UES GMW is the average  
gram  
molecular weight of the unsaturated ester, UES Mass is the mass  
of the  
unsaturated ester, and UES C.dbd.C is the average number of  
double bonds  
per unsaturated ester molecule. In some embodiments, the  
\*\*\*mercaptan\*\*\* to carbon-carbon double bond molar ratio is  
greater  
than 0.25. In other embodiments, the \*\*\*mercaptan\*\*\* to  
carbon-carbon double bond molar ratio is greater than 0.5;  
alternatively, greater than 0.75; alternatively, greater than 1;  
alternatively, greater than 1.25; or alternatively, greater than  
1.5. In  
other embodiments, the \*\*\*mercaptan\*\*\* to carbon-carbon  
double bond  
molar ratio can range from 0.25 to 2; alternatively, from 0.5 to  
1.5, or  
alternatively, from 0.75 to 1.25.

DETD In some aspects the reaction between the \*\*\*mercaptan\*\*\* and  
the  
unsaturated ester is catalyzed. The reaction of the  
\*\*\*mercaptan\*\*\*  
and the unsaturated ester can be catalyzed by a heterogeneous  
catalyst

or homogeneous catalyst, as described herein. In some aspects, the reaction between the \*\*\*mercaptan\*\*\* and the unsaturated ester is initiated by a free radical initiator or ultraviolet radiation, as described herein.

DETD The free radical initiator can be any free radical initiator capable of forming free radicals under thermal or light photolysis. Generally, the free radical initiator is selected from the general class of compounds having a --N.dbd.N-- group or a --O--O-- group. Specific classes of free radical initiators include diazo compounds, dialkyl peroxides, hydroperoxides, and peroxy esters. Specific initiators include azobenzene, 2,2'-azobis(2-methylpropionitrile, 4,4'-azobis(4-cyanovaleric acid), 1,1'-azobis(cyclohexanecarbonitrile), 2,2'-azobis(2methylpropane), 2,2'-azobis(2-methylpropionamidine) dihydro-chloride, methylpropionitrile, azodicarboxamide, tert-butyl hydroperoxide, di-tert-butyl peroxide, octylperbenzoate. In some embodiments, the free radical initiated reaction of the \*\*\*mercaptan\*\*\* and the unsaturated ester is performed at a reaction temperature within  $\pm 50^{\circ}\text{C}$ . of the 1 hour half life of the free radical initiator. In other embodiments, the reaction temperature is within  $\pm 25^{\circ}\text{C}$ . of the 1 hour half life of the free radical initiator; alternatively, the reaction temperature is within  $\pm 20^{\circ}\text{C}$ . of the 1 hour half life of the free radical initiator; alternatively, the reaction temperature is within  $\pm 15^{\circ}\text{C}$ . of the 1 hour half life of the free radical initiator; or alternatively, the reaction temperature is within  $\pm 10^{\circ}\text{C}$ . of the 1 hour half life of the free radical initiator. In embodiments where the free radical initiated reaction of the \*\*\*mercaptan\*\*\* and the unsaturated ester is initiated by light photolysis, the light can be any light capable creating free radicals. In some embodiments, the light is UV radiation. Other sources of light capable of creating free radicals will be apparent to those of skill in the art and are to be considered within the scope of the present invention.

DETD In another aspect, the reaction of the \*\*\*mercaptan\*\*\* and the unsaturated ester is initiated by UV radiation. In these embodiments, the UV radiation may be any UV radiation capable of initiating the reaction of the \*\*\*mercaptan\*\*\* and the unsaturated ester. In

some

embodiments, the UV radiation is generated by a medium pressure mercury lamp.

DETD The reaction of the \*\*\*mercaptan\*\*\* and the unsaturated ester can occur in a batch reactor or a continuous reactor. Any of the batch or continuous reactors described herein can be used in this reaction. Other suitable reactors will be apparent to those of skill in the art and are

to be considered within the scope of the present invention. DETD The reaction time for reacting the \*\*\*mercaptan\*\*\* and the unsaturated ester can be any time required to form the sulfide-containing ester. Generally, the reaction time is at least 5 minutes. In some embodiments, the reaction time ranges from 5 minutes to 72 hours; alternatively, from 10 minutes to 48 hours; or alternatively, from 15 minutes to 36 hours.

DETD In some embodiments, the process to produce the sulfide-containing ester further comprises a step to remove any residual \*\*\*mercaptan\*\*\* that remains after reacting the \*\*\*mercaptan\*\*\* and the unsaturated ester. In some embodiments, the sulfide-containing ester is vacuum stripped to remove the residual \*\*\*mercaptan\*\*\*. In some embodiments, the sulfide-containing ester is vacuum stripped at a temperature between 25.degree. C. and 250.degree. C.; or alternatively, between 50.degree. C. and 200.degree. C. In other embodiments, the sulfide-containing ester is sparged with an inert gas to remove the residual \*\*\*mercaptan\*\*\*. In some embodiments, the sulfide-containing ester is sparged with an inert gas at a temperature between 25.degree. C. and 250.degree. C.; or alternatively, between 50.degree. C. and 200.degree. C. In some aspects, the inert gas is nitrogen. Generally, the stripped or sparged sulfide-containing ester comprises less than 5 weight percent of the \*\*\*mercaptan\*\*\*. In other embodiments, the stripped or sparged sulfide-containing ester comprises less than 2 weight percent of the \*\*\*mercaptan\*\*\*; alternatively, less than 1 weight percent of the \*\*\*mercaptan\*\*\*; or alternatively, less than 0.5 weight percent of the \*\*\*mercaptan\*\*\*.

DETD The reaction between the \*\*\*mercaptan\*\*\* and the unsaturated ester can be performed at any temperature capable of forming the sulfide-containing ester. In some embodiments, the

\*\*\*mercaptan\*\*\*

and the unsaturated ester can be reacted at a reaction temperature of greater than -20.degree. C. In other embodiments, the reaction temperature is greater than 0.degree. C.; alternatively, greater than

20.degree. C.; alternatively, greater than 50.degree. C.;

alternatively,

greater than 80.degree. C.; or alternatively, greater than 100.degree.

C. In yet other embodiments, the \*\*\*mercaptan\*\*\* and the unsaturated

ester can be reacted at a temperature from -20.degree. C. to 250.degree.

C.; alternatively, from 20.degree. C. to 200.degree. C.; or

alternatively, from 80.degree. C. to 160.degree. C.

DETD The reaction between the \*\*\*mercaptan\*\*\* and the unsaturated ester

can be performed at any pressure that maintains the

\*\*\*mercaptan\*\*\*

and the unsaturated ester in a substantially liquid state. In

some

embodiments, the \*\*\*mercaptan\*\*\* and the unsaturated ester

can be

performed at a reaction pressure ranging from 0 psig to 2000

psig. In

other embodiments, the reaction pressure ranges from 0 psig to

1000

psig; alternatively, from 0 psig to 500 psig; or alternatively,

from 0

psig to 200 psig.

DETD Using the disclosed process, sulfide-containing ester having a low

carbon-carbon double bond to sulfide group molar ratio can be produced.

In an aspect, the process for producing the sulfide-containing ester

forms a sulfide-containing ester having a carbon-carbon double bond to

\*\*\*thiol\*\*\* group molar ratio of less than 1.5. Additional

carbon-carbon double bond to sulfide group molar ratios are

disclosed

herein.

DETD As another embodiment of the present invention, another process for

producing a class of sulfide-containing esters, which includes hydroxy

sulfide-containing esters, is advantageously provided. In this embodiment, the hydroxy sulfide-containing esters and hydroxy sulfide-containing ester compositions can be produced by a

process

comprising the steps of contacting a \*\*\*mercaptan\*\*\* and an epoxidized unsaturated ester and reacting the \*\*\*mercaptan\*\*\*

and

the epoxidized unsaturated ester to produce or form the hydroxy sulfide-containing ester. The process can be applied to any

\*\*\*mercaptan\*\*\* and/or any epoxidized unsaturated esters

described

herein. The process for producing the hydroxy sulfide-containing

ester

can also include any additional process steps or process conditions as described herein. Additionally, the process for producing the hydroxy sulfide-containing ester can form any hydroxy sulfide-containing ester as described herein.

DETD In some aspects, the reaction between the \*\*\*mercaptan\*\*\* and the unsaturated ester occurs in the presence of a solvent. In other aspects the reaction between the \*\*\*mercaptan\*\*\* and the unsaturated ester occurs in the substantial absence of a solvent. When the reaction occurs in the presence of a solvent, the solvent is selected from an aliphatic hydrocarbon, an ether, an aromatic compound, or any combination thereof. Generally, the solvent, regardless of its chemical class, can comprise from 1 to 20 carbon atoms; alternatively, from 3 to 10 carbon atoms. When the solvent includes an aliphatic hydrocarbon, the aliphatic hydrocarbon is butane, isobutane, pentane, hexane, heptane, octane, or any mixture thereof. When the solvent includes an aromatic compound, the aromatic compound is benzene, toluene, xylene, ethylbenzene, or any mixture thereof. When the solvent includes an ether, the ether is diethyl ether, dipropyl ether, tetrahydrofuran, or any mixture thereof.

DETD When a solvent is used for the reaction between the \*\*\*mercaptan\*\*\* and the epoxidized unsaturated ester, the quantity of solvent can be any amount that facilitates the reaction, as understood by those of skill in the art. In some embodiments, the mass of the solvent is less than 30 times the mass of the epoxidized unsaturated ester. In other embodiments, the mass of the solvent is less than 20 times the mass of the epoxidized unsaturated ester; alternatively, less than 15 times the mass of the epoxidized unsaturated ester; alternatively, less than 10 times the mass of the epoxidized unsaturated ester; or alternatively, less than 5 times the mass of the epoxidized unsaturated ester. In other embodiments, the mass of the solvent is from 2 times to 20 times the mass of the epoxidized unsaturated ester; alternatively, from 3 times to 15 times the mass of the epoxidized unsaturated ester; alternatively, from 4 times to 15 times the mass of the epoxidized unsaturated ester;

or alternatively, from 5 times to 10 times the mass of the epoxidized unsaturated ester.

DETD The reaction of the \*\*\*mercaptan\*\*\* and the epoxidized unsaturated ester can occur using any \*\*\*mercaptan\*\*\* to molar equivalents of \*\*\*epoxide\*\*\* groups in the epoxidized unsaturated ester (hereinafter referred to as " \*\*\*mercaptan\*\*\* to \*\*\*epoxide\*\*\* group molar ratio") that is capable of producing the herein described .alpha.-hydroxy \*\*\*thiol\*\*\* esters. The molar equivalents of epoxidized unsaturated ester epoxidized groups can be calculated by the equation: ##EQU4##

DETD In this equation, EUES GMW is the average gram molecular weight of the epoxidized unsaturated ester, EUES Mass is the mass of the epoxidized unsaturated ester, and EUES \*\*\*Epoxide\*\*\* is the average number of \*\*\*epoxide\*\*\* groups per epoxidized unsaturated ester molecule. In some embodiments, the \*\*\*mercaptan\*\*\* to \*\*\*epoxide\*\*\* group molar ratio is greater than 0.2. In other embodiments, the \*\*\*mercaptan\*\*\* to \*\*\*epoxide\*\*\* group molar ratio is greater than 0.5; alternatively, greater than 1; or alternatively, greater than 2. In other embodiments, the hydrogen sulfide to \*\*\*epoxide\*\*\* group molar ratio ranges from 0.2 to 10; alternatively, from 0.5 to 8; alternatively, from 0.75 to 5; or alternatively, from 1 to 3.

DETD In some aspects, the reaction of the \*\*\*mercaptan\*\*\* and the epoxidized unsaturated ester occurs in the presence of a catalyst. Generally, the catalyst is any catalyst that is capable of catalyzing the reaction of the \*\*\*mercaptan\*\*\* and the epoxidized unsaturated ester to produce the desired hydroxy \*\*\*thiol\*\*\* ester. In one aspect, the catalyst is selected from the group consisting of homogeneous and heterogeneous catalysts. In other aspects, the catalyst is selected from the group consisting of zeolites, heterogeneous catalysts, homogeneous catalysts, and mixtures thereof. In another aspect, the catalyst is an amine. In other aspects, the catalyst is selected from the group consisting of cyclic conjugated amines, 1,8-diazabicyclo[5.4.0]undec-7-ene, 1,5-diazabicyclo[4.3.0]non-5-ene, and mixtures thereof.

DETD In some aspects, the reaction of the \*\*\*mercaptan\*\*\* and the epoxidized unsaturated ester occurs in the presence of a catalyst. Generally, the catalyst is any catalyst that is capable of

catalyzing  
the reaction of the \*\*\*mercaptan\*\*\* and the epoxidized  
unsaturated  
ester to produce the desired hydroxy \*\*\*thiol\*\*\* ester. In  
some  
embodiments the catalyst is an organic base. In some embodiments,  
the  
catalyst can be 1,8-diazabicyclo[5.4.0]undec-7-ene. (What other  
catalysts may be used?)  
DETD The reaction of the \*\*\*mercaptan\*\*\* and the epoxidized  
unsaturated  
ester can occur in a batch reactor or a continuous reactor. Any  
of the  
batch or continuous reactors described herein can be used in this  
reaction. Other suitable reactors will be apparent to those of  
skill in  
the art and are to be considered within the scope of the present  
invention.  
DETD The time required for the reaction of the \*\*\*mercaptan\*\*\*  
and the  
epoxidized unsaturated ester can be any reaction time required to  
form  
the described hydroxy sulfide-containing ester. Generally, the  
reaction  
time is at least 15 minutes. In some embodiments, the reaction  
time  
ranges from 15 minutes to 72 hours; alternatively, from 30  
minutes to 48  
hours; or alternatively, from 45 minutes to 36 hours.  
DETD In some embodiments, the process to produce the hydroxy  
sulfide-containing ester further comprises a step to remove the  
residual  
\*\*\*mercaptan\*\*\* after reacting the \*\*\*mercaptan\*\*\* and  
the  
epoxidized unsaturated ester. In some embodiments the hydroxy  
sulfide-containing ester is vacuum stripped. In some embodiments,  
the  
hydroxy sulfide-containing ester is vacuum stripped at a  
temperature  
between 25.degree. C. and 250.degree. C.; or alternatively,  
between  
50.degree. C. and 200.degree. C. In other embodiments, the  
hydroxy  
sulfide-containing ester is sparged with an inert gas to remove  
the  
\*\*\*mercaptan\*\*\*. In some embodiments, the hydroxy sulfide-  
containing  
ester is sparged with an inert gas at a temperature between  
25.degree.  
C. and 250.degree. C.; or alternatively, between 50.degree. C.  
and  
200.degree. C. In some aspects, the inert gas is nitrogen.  
Generally,  
the stripped or sparged hydroxy sulfide-containing ester  
comprises less  
than 5 weight percent of the \*\*\*mercaptan\*\*\*. In other  
embodiments,  
the stripped or sparged hydroxy sulfide-containing ester  
comprises less  
than 2 weight percent of the \*\*\*mercaptan\*\*\*; alternatively,

less than 1 weight percent of the \*\*\*mercaptan\*\*\* ; or alternatively, less than 0.5 weight percent of the \*\*\*mercaptan\*\*\* .

DETD The reaction between the \*\*\*mercaptan\*\*\* and the epoxidized unsaturated ester can be performed at any reaction temperature capable of forming the hydroxy sulfide-containing ester. In some embodiments, the reaction temperature is greater than -20.degree. C. In other embodiments, the reaction temperature is greater than 0.degree. C.; alternatively, greater than 20.degree. C.; alternatively, greater than 50.degree. C.; or alternatively, greater than 80.degree. C. In yet other embodiments, the reaction temperature ranges from -20.degree. C. to 200.degree. C.; alternatively, from 20.degree. C. to 170.degree. C.; or alternatively, from 80.degree. C. to 140.degree. C.

DETD The reaction between the \*\*\*mercaptan\*\*\* and the epoxidized unsaturated ester can be performed at any reaction pressure that maintains the \*\*\*mercaptan\*\*\* and the epoxidized unsaturated ester in a substantially liquid state. In some embodiments, the reaction pressure ranges from 0 psig to 2000 psig. In other embodiments, the reaction pressure ranges from 0 psig to 1000 psig; alternatively, from 0 psig to 500 psig; or alternatively, from 0 psig to 200 psig.

DETD In another aspect, the process to produce a hydroxy sulfide-containing ester produces a hydroxy sulfide-containing ester having an \*\*\*epoxide\*\*\* group to sulfide group molar ratio less than 2.

Other hydroxy sulfide-containing ester \*\*\*epoxide\*\*\* group to sulfide group molar ratios are described herein. (The next passage needs to be incorporated into the hydroxy \*\*\*thiol\*\*\* ester section along with the first sentence of this paragraph.) Alternatively, the hydroxy sulfide-containing ester \*\*\*epoxide\*\*\* group to \*\*\*thiol\*\*\* group molar ratio can be less than 1.5; alternatively, less than 1.0; alternatively, less than 0.5; alternatively, less than 0.25; or alternatively, less than 0.1. In other embodiments, the hydroxy sulfide-containing ester can be substantially free of \*\*\*epoxide\*\*\* groups.

DETD As an embodiment of the present invention, processes for producing a sulfonic acid-containing ester and for producing a sulfonate-containing ester are advantageously provided. Generally, the process for producing the sulfonic acid-containing ester comprises the steps of contacting a



\*\*\*thiol\*\*\* ester and an oxidizing agent and oxidizing at least one \*\*\*thiol\*\*\* group of the \*\*\*thiol\*\*\* ester to produce a sulfonic acid group. The process for producing the sulfonate-containing ester comprises the steps of contacting a sulfonic acid-containing ester with a base and forming a sulfonate-containing ester.

DETD In an embodiment, the process to prepare a sulfonic acid-containing ester comprises the steps of contacting the \*\*\*thiol\*\*\* ester and the oxidizing agent and oxidizing the \*\*\*thiol\*\*\* ester to produce the sulfonic acid-containing ester. Generally the oxidizing agent oxidizes at least one \*\*\*thiol\*\*\* group of the \*\*\*thiol\*\*\* ester to a sulfonate group. The process to produce the sulfonic acid-containing ester composition can be applied to any \*\*\*thiol\*\*\* ester described herein to prepare any sulfonic acid-containing ester described herein. In some embodiments, the \*\*\*thiol\*\*\* ester includes a hydroxy group. For example, the \*\*\*thiol\*\*\* ester can be any hydroxy \*\*\*thiol\*\*\* ester described herein. The oxidizing agent can be any oxidizing agent described herein.

DETD In some aspects, the oxidation of the \*\*\*thiol\*\*\* ester occurs in the presence of a solvent. In some aspects, the solvent is water.

DETD The oxidizing agent that is contacted with the \*\*\*thiol\*\*\* ester can be any oxidizing agent capable of oxidizing a \*\*\*thiol\*\*\* group to a sulfonic acid group. In some embodiments, the oxidizing agent is oxygen. In other embodiments, the oxidizing agent is chlorine. In other embodiments, the oxidizing agent is dimethyl sulfoxide. In yet other embodiments, the oxidizing agent is a combination of a hydrogen halide and a catalytic amount of a dialkyl sulfide, such as dimethyl sulfoxide.

Other suitable oxidizing agents will be apparent to those of skill in the art and are to be considered within the scope of the present invention.

DETD The oxidation of the \*\*\*thiol\*\*\* ester can be performed at any temperature capable of converting the \*\*\*thiol\*\*\* ester to a sulfonic acid-containing ester. In some embodiments, the \*\*\*thiol\*\*\* ester is oxidized a temperature greater than -20.degree. C. In other embodiments, the \*\*\*thiol\*\*\* ester is oxidized at a temperature greater than 0.degree. C.; alternatively, greater than 20.degree.

C.; or  
alternatively, greater than 50.degree. C.

DETD The time required for the oxidation of the \*\*\*thiol\*\*\* ester can be any time required to form the desired sulfonic acid-containing ester. Generally, the time required for the oxidation of the \*\*\*thiol\*\*\* ester is at least 15 minutes; alternatively, at least 30 minutes; alternatively, at least 45 minutes; or alternatively, at least 1 hour. In some embodiments, the time required for the oxidation of the \*\*\*thiol\*\*\* ester ranges from 15 minutes to 12 hours; alternatively, from 30 minutes to 6 hours; alternatively, from 45 minutes to 3 hours.

DETD The oxidation of the \*\*\*thiol\*\*\* ester can be performed at any pressure that maintains the \*\*\*thiol\*\*\* ester and the oxidation agent in the proper state, which is not always a liquid state, to oxidize the \*\*\*thiol\*\*\* ester to a sulfonic acid-containing ester. For example, when the oxidation agent is chlorine, the chlorine can be in the gaseous state. In some embodiments, the oxidation of the \*\*\*thiol\*\*\* ester can be performed at a pressure ranging from 0 psig to 2000 psig. In other embodiments, the oxidation of the \*\*\*thiol\*\*\* ester can be performed at a pressure ranging from 0 to 1000 psig; or alternatively, 0 to 500 psig.

DETD The oxidation of the \*\*\*thiol\*\*\* ester can be performed in a batch reactor or a continuous reactor, as described herein. Additionally, the process to produce the sulfonic acid-containing ester can comprise additional process steps as recognized by those skilled in the art.

DETD The formation of the sulfonate-containing ester can be performed at any temperature capable of converting the sulfonic acid group of the sulfonic acid-containing ester to a sulfonate group. In some embodiments, the sulfonate-containing ester is formed at a temperature greater than -20.degree. C. In other embodiments, the \*\*\*thiol\*\*\* ester is oxidized at a temperature greater than 0.degree. C.; alternatively, greater than 20.degree. C.; or alternatively, greater than 50.degree. C. In yet other embodiments, the \*\*\*thiol\*\*\* ester is oxidized at a temperature ranging from 0.degree. C. to 250.degree. C.; alternatively, from 0.degree. C. to 150.degree. C.; or alternatively, from 20.degree. C. to 100.degree. C.

DETD A preferred sulfur-containing vegetable oil is MVO available from

Chevron Phillips Chemical Co. under the tradename Polymercaptan 358.

Polymercaptan 358 is made by the free radical addition of hydrogen sulfide to the double bonds in soybean oil. Typically, Polymercaptan 358

has a \*\*\*thiol\*\*\* sulfur content of 5 to 10% and equivalent weights of 640 to 320, respectively.

DETD Another preferred sulfur-containing vegetable oil useful as part of the

isocyanate-reactive component is a MHVO such as mercapto-hydroxy soybean

oil. As described herein, a preferred mercapto-hydroxy soybean oil is

made by the free radical addition of hydrogen sulfide to epoxidized

soybean oil. Typically, the mercapto and hydroxy functionalities are

equal and the \*\*\*mercaptan\*\*\* content is about 8.3% \*\*\*thiol\*\*\*

sulfur. The equivalent weight of this material is 192, which includes

both mercapto and hydroxy functionalities.

DETD Yet another preferred sulfur-containing vegetable oil useful as part of

the isocyanate-reactive component is a CMVO such as sulfur cross-linked

mercaptanized soybean oil. Sulfur cross-linked mercaptanized soybean oil

is made by the addition of elemental sulfur to mercaptanized soybean

oil. In this process, a portion of the \*\*\*mercaptan\*\*\* groups are

consumed as cross-linking sites for the sulfur. Typical sulfur cross-linked mercaptanized soybean oil products by Chevron

Phillips

Chemical Co. include Runs #22, 194, 195, 196 and 197 and have a \*\*\*thiol\*\*\* sulfur content ranging from about 8.0% to 1.4%

and

equivalent weights ranging from about 400 to about 2250, respectively.

DETD For epoxy polymer encapsulated CRF material made from sulfur-containing

vegetable oil, it has been found that the use of a tertiary amine catalyst is highly preferred. The amount used is such to be

sufficient

to give the desired reaction rate for the production of the encapsulated

slow release fertilizer product. A non-limiting example of a suitable

amine catalyst is diazobicycloundecacene also known as

1,8-diazabicyclo[5,4,0]undec-7-ene [CAS# \*\*\*6674-22-2\*\*\* ] or "DBU",

which is preferably used in the range of about 0.1% to 0.5% by weight of

the coating. Other suitable catalyst materials will be apparent to those

of ordinary skill in the art.

DETD The preferred sulfur-containing vegetable oil to be used in

production

of an epoxy polymer coated CRF material is MHVO such as mercapto-hydroxy

soybean oil. One such material is mercapto-hydroxy soybean oil known as

MHSO 566-84 produced by Chevron Phillips Chemical Co. This preferred

material contains 8.33% \*\*\*thiol\*\*\* sulfur, with an equivalent

weight of 384, based upon the \*\*\*mercaptan\*\*\* functionality. DETD The unsaturated ester used as a feedstock to produce the

\*\*\*thiol\*\*\*

ester compositions described herein can be described using a number of

different methods. One method of describing the unsaturated ester feedstock is by the number of ester groups and the number of carbon-carbon double bonds that comprise each unsaturated ester

oil

molecule. Suitable unsaturated ester used as a feedstock to produce the

\*\*\*thiol\*\*\* ester compositions described herein minimally comprise at

least 1 ester group and at least 1 carbon-carbon double bond.

However,

beyond this requirement, the number of ester groups and carbon-carbon

double bonds comprising the unsaturated esters are independent elements

and can be varied independently of each other. Thus, the

unsaturated

esters can have any combination of the number of ester groups and the

number of carbon-carbon double bonds described separately herein. Suitable, unsaturated esters can also contain additional

functional

groups such as alcohol, aldehyde, ketone, epoxy, ether, aromatic groups,

and combinations thereof. As an example, the unsaturated esters can also

comprise hydroxy groups. An example of an unsaturated ester that contains hydroxy groups is castor oil. Other suitable unsaturated

esters

will be apparent to those of skill in the art and are to be considered

within the scope of the present invention.

DETD In yet another aspect, the polyol or mixture of polyols used to produce

the unsaturated \*\*\*thiol\*\*\* ester has a molecular weight or average

molecular weight less than 500. In other embodiments, the polyol or

mixture of polyols have a molecular weight or average molecular

weight less than 300; alternatively less than 200; alternatively, less

than 150; or alternatively, less than 100.

DETD Specific carboxylic acids used as a component of the carboxylic acid

composition used to produce the unsaturated ester oil can have from 3 to

30 carbon atoms per carboxylic acid molecule. In some embodiments the carboxylic acid is linear. In some embodiments the carboxylic acid is branched. In some embodiments the carboxylic acid is a mixture of linear and branched carboxylic acids. In some embodiments the carboxylic acid can also comprise additional functional groups including alcohols, aldehydes, ketones, and \*\*\*epoxides\*\*\*, among others.

DETD Minimally, the epoxidized unsaturated ester comprises at least one \*\*\*epoxide\*\*\* group. In an embodiment the epoxidized unsaturated ester comprises at least 2 \*\*\*epoxide\*\*\* groups; alternatively, at least 3 \*\*\*epoxide\*\*\* groups; or alternatively, at least 4 \*\*\*epoxide\*\*\* groups; or alternatively, from 2 to 9 \*\*\*epoxide\*\*\* groups; alternatively, from 2 to 4 \*\*\*epoxide\*\*\* groups; alternatively, from 3 to 8 \*\*\*epoxide\*\*\* groups; or alternatively, from 4 to 8 \*\*\*epoxide\*\*\* groups.

DETD In some embodiments, the unsaturated ester comprises a mixture of epoxidized unsaturated esters. In this aspect, the number of \*\*\*epoxide\*\*\* groups in the epoxidized unsaturated ester is best described as an average number of \*\*\*epoxide\*\*\* groups per epoxidized unsaturated ester molecule. In some embodiments, the epoxidized unsaturated esters have an average of at least 1.5 \*\*\*epoxide\*\*\* groups per epoxidized unsaturated ester molecule; alternatively, an average of at least 2 \*\*\*epoxide\*\*\* groups per epoxidized unsaturated ester molecule; alternatively, an average of at least 2.5 \*\*\*epoxide\*\*\* groups per epoxidized unsaturated ester molecule; or alternatively, an average of at least 3 \*\*\*epoxide\*\*\* groups per epoxidized unsaturated ester molecule. In other embodiments, the epoxidized unsaturated esters have average of from 1.5 to 9 \*\*\*epoxide\*\*\* groups per epoxidized unsaturated ester molecule; alternatively, an average of from 3 to 8 \*\*\*epoxide\*\*\* groups per epoxidized unsaturated ester molecule; alternatively, an average of from 2 to 4 \*\*\*epoxide\*\*\* groups per epoxidized unsaturated ester molecule; or alternatively, from of 4 to 8 \*\*\*epoxide\*\*\* groups per epoxidized unsaturated ester molecule.

DETD The \*\*\*thiol\*\*\* composition can include an average of greater than 0 to about 4 \*\*\*epoxide\*\*\* groups per triglyceride. The \*\*\*thiol\*\*\* composition can also include an average of

greater than

1.5 to about 9 \*\*\*epoxide\*\*\* groups per triglyceride.

DETD \*\*\*Mercaptans\*\*\*

DETD Within some embodiments, an unsaturated ester or an epoxidized unsaturated ester is contacted with \*\*\*mercaptan\*\*\*. Within these

embodiments, the \*\*\*mercaptan\*\*\* can be any \*\*\*mercaptan\*\*\* comprising from 1 to 20 carbon atoms. Generally, the

\*\*\*mercaptan\*\*\*

can have the following structure:  $\text{HS}-\text{R}$  wherein R3 is a C1 to

C20 organyl groups or a C1 to C20 hydrocarbyl groups. In further embodiments the R3 can be a C2 to C10 organyl group or a C2 to

C10

hydrocarbyl group. In some embodiments, the \*\*\*mercaptan\*\*\* composition comprises a solvent. In one aspect, the

\*\*\*mercaptan\*\*\*

composition comprises at least one other functional group.

DETD The at least one other functional group can be selected from several

different groups. For example, the at least one other functional group

is an alcohol group, a carboxylic alcohol group, a carboxylic ester

group, an amine group, a sulfide group, a \*\*\*thiol\*\*\* group, a

methyl or ethyl ester of a carboxylic acid group, or combinations thereof. Other types of functional groups will be apparent to

those of

skill in the art and are to be considered within the scope of the present invention.

DETD In some embodiments, the \*\*\*mercaptan\*\*\* is selected from the group

consisting of 3-mercaptopropyl-trimethoxysilane, 2-mercaptopyridine,

4-mercaptopyridine, 2-mercaptopyrimidine, mercaptopyruvic acid, mercaptosuccinic acid, 2-mercaptopyridine, 6-

mercaptopyridine

acid, 2-mercaptopyridine, 4-mercaptopyridine, 3-mercaptopyridine,

propanediol,

3-mercaptopyridine, 3-mercaptopyridine, 1-mercaptopyridine,

1-mercaptopyridine, 3-mercaptopyridine, 2-mercaptopyridine,

acid,

3-mercaptopyridine, 2-mercaptopyridine, 2-mercaptopyridine,

3-mercaptopyridine, 4-mercaptopyridine, 2-

mercaptopyridine

acid, 2-mercaptopyridine, 2-mercaptopyridine, 2-mercaptopyridine,

sulfide,

16-mercaptopyridine, 6-mercaptopyridine,

4'-mercaptopyridine, mercaptopyridine, 2-mercaptopyridine,

acid,

3-mercaptopyridine, 4-mercaptopyridine, 2-

mercaptopyridine,

3-mercaptopyridine, 11-mercaptopyridine, 11-mercaptopyridine,

11-mercaptopyridine, or combinations thereof.

DETD In some embodiments, the \*\*\*mercaptan\*\*\* is selected from the group

consisting of beta-mercaptopyridine, 2-mercaptopyridine, 3-

mercaptopyridine,

4-mercaptopyridine, 1-mercaptopyridine, 1-mercaptopyridine,

mercaptoacetic acid, 2-mercaptopropionic acid, 3-mercaptopropionic acid, 2-mercaptobenzoic acid, 3-mercaptobenzoic acid, 4-mercaptobenzoic acid, 2-mercaptobenzylalcohol, 3-mercapto-2-butanol, 4-mercapto-1-butanol, 2-mercaptoethyl ether, 2-mercaptoethyl sulfide, 6-mercapto-hexanol, 3-mercapto-1,2-propanediol, mercaptosuccinic acid, and mixtures thereof.

In further embodiments, the \*\*\*mercaptan\*\*\* is selected from the

group consisting of beta-mercaptoethanol, 1-mercapto-2-propanol, 1-mercapto-3-propanol, 2-mercaptobenzylalcohol, 3-mercapto-2-butanol,

4-mercapto-1-butanol, 6-mercapto-hexanol, 3-mercapto-1,2-propanediol,

and mixtures thereof. In further embodiments, the \*\*\*mercaptan\*\*\* is

selected from the group consisting 2-mercaptophenol, 3-mercaptophenol,

4-mercaptophenol, and mixtures thereof. In yet further embodiments, the

\*\*\*mercaptan\*\*\* is selected from the group consisting mercaptoacetic

acid, 2-mercaptopropionic acid, 3-mercaptopropionic acid, 2-mercaptobenzoic acid, 3-mercaptobenzoic acid, 4-mercaptobenzoic acid,

mercaptosuccinic acid, and mixtures thereof.

DETD Within some embodiments, the inventive compositions described herein

are reacted with an isocyanate compound to produce a polythiourethane

composition. The isocyanate may be any isocyanates capable of reacting

with the \*\*\*thiol\*\*\* esters, hydroxy \*\*\*thiol\*\*\* esters, and a

cross-linked \*\*\*thiol\*\*\* esters described herein to form a polyurethane composition. Generally, the isocyanate compound has

at

least two isocyanate groups.

DETD In order to quantitatively measure the \*\*\*thiol\*\*\* sulfur, the

\*\*\*thiol\*\*\* sulfur analyses were conducted using silver nitrate

titration in accordance with ASTM D3227, with the following modifications designed to minimize probe fouling by silver salts:

the

samples were diluted in a known mass of tetrahydrofuran. The

silver

nitrate concentration was 0.01 N standardized against potassium iodide.

DETD \*\*\*Thiol\*\*\* sulfur was analyzed by three different tests.

The first

test used was the modified ASTM D3227, which resulted in a

\*\*\*thiol\*\*\*

sulfur measurement of 4.64%. The second test used to measure the

\*\*\*thiol\*\*\* sulfur was SLP-1204, which is a test developed by

Chevron

Phillips Chemical Company LLP. By using the SLP-1204 test, the

resulting  
 \*\*\*thiol\*\*\* sulfur measurement was 4.28%. Lastly, the total sulfur was measured by combustion analysis, which resulted in a total sulfur measurement of 4.27%.  
 DETD Vegetable oil (42 kg) was charged to a 100-gallon holding vessel. The vessel was purged with nitrogen and returned to atmospheric pressure. Hydrogen sulfide (174 kg) was charged to the holding vessel. The vessel temperature was controlled from 25-30.degree. C. while the pressure was typically maintained between 380-400 psig. The reactants were continuously rolled from the holding tank through a stainless steel tubular photochemical reactor containing a 7.5 KW Hanovia medium pressure mercury lamp contained within a quartz tube. Reactor temperature, pressure, and composition were monitored over the course of the reaction. The reaction time was dependent upon reaching a desired composition of \*\*\*thiol\*\*\* sulfur. Upon completion, the unreacted hydrogen sulfide was slowly vented from the system. Residual H.sub.2S was removed at 100.degree. C. and reduced pressure while passing nitrogen through a nitrogen sparge tube. The product was drained from the bottom of the reactor into a clean drum. The \*\*\*thiol\*\*\* sulfur measurements were 11.0% when using the modified ASTM D3227, 8.74% when using SLP-1204, and the total sulfur was 11.21% when using combustion analysis (total sulfur).  
 DETD The resulting mercaptanized soybean oil was subjected to nitrogen sparging under reduced pressure at 100.degree. C. for a period of 4 hours to remove any residual hydrogen sulfide. The \*\*\*thiol\*\*\* sulfur measurements were 13.0% when using the modified ASTM D3227, 9.82% when using SLP-1204, and 11.69% when using combustion analysis.  
 DETD Table 1 provides the properties of the mercaptanized soybean oil produced in examples 1-3.  
 TABLE 1

#### Mercaptanized Soybean Oil Product Properties

Cyclic Sulfide to ***Thiol***			
***Thiol*** Sulfur.sup..dagger. Group			
C.dbd.C	to	groups	
Example	***Thiol*** (wt %)	Molar Ratio	Molar Ratio
1	4.28	0.02	2.79
2	11.0	0.03	0.26
3	13.0	0.03	0.51



.sup..dagger. \*\*\*Thiol\*\*\* sulfur content determined by the modified ASTM D3227

DETD Soybean oil was charged to a 1000 gallon stirred reactor. Hydrogen sulfide was then charged to the reactor. After the hydrogen sulfide was charged to the reactor, the stirrers and the UV lamps were turned on and the reaction allowed to build temperature and pressure as the reaction proceed. The reaction was continued until a minimum \*\*\*thiol\*\*\* sulfur content of 8 weight percent was achieved. After reaction was completion, the excess hydrogen sulfide was flashed from the reactor.

For runs 2-5, the mercaptanized soybean oil product underwent an additional hydrogen sulfide stripping step comprising stripping hydrogen sulfide from the product under vacuum, 50 mm Hg, at 250.degree.

F. (only true for runs 2-5).

DETD Table 3 provides the details of the analysis of the mercaptanized soybean oil producing in the five 1000 gallon reactor runs.

TABLE 3

1000 gallon reactor Mercaptanized Soybean Oil Product Properties				
		Side Chain		
		***Thiol***	Cyclic Sulfide to	***Thiol*** C.dbd.C
to				
		***Thiol***	Containing	
Run		Sulfur.sup..dagger. Group		groups
		***Thiol***	Groups	
Number	(wt %)	Molar Ratio	Molar Ratio	(%)
1	9.3	--	--	71.6
2	9.6	0.04	0.48	72.3
3	9.2	0.03	0.59	69.1
4	9.3	0.03	0.62	71.6
5	10.1	0.03	0.54	72.3

.sup..dagger. \*\*\*Thiol\*\*\* sulfur content determined by Raman spectroscopy

Mercaptanized Castor Bean Oil

DETD The analytical properties of the two mercaptanized castor oil products are provide in Table 4.

TABLE 4

Mercaptanized Castor Oil Product Properties				
		***Thiol***	Side Chain	
		Containing		
		Sulfur.sup..dagger. C.dbd.C to	***Thiol***	groups
		***Thiol***	Groups	
Example	(wt %)	Molar Ratio	(%)	
1	6.4	0.52	64.1	

2

7.4

0.26

77.7

.sup..dagger. \*\*\*Thiol\*\*\* sulfur content determined by Raman spectroscopy

Mercaptohydroxy Soybean Oil Synthetic Procedure

DETD Epoxidized Soybean Oil (700 g, .about.0.7 mol) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 4.7 g, 30.5 mmol) were charged to a 1-L Hastelloy C autoclave reactor that was pressure tested to 630 psig. Hydrogen sulfide (H.sub.2S, 132.0 g, 3.87 mol) was then pressured into the stirred reactor contents through a dip tube in the liquid space. The reaction mixture was heated and maintained at 85.degree. C. with stirring for 8 hrs, during which time the reactor pressure decreased from a maximum of 351 psig to 219 psig. The stirrer was stopped and while still warm (80-85.degree. C.), excess H.sub.2S was slowly vented to a low-pressure flare. The reactor vapor space was then swept with N.sub.2 for 1 hr and the reactor contents drained warm (80-85.degree. C.). The reaction product was N.sub.2 sparged under vacuum (<5 mmHg) at 130-140.degree. C. for 16 hrs to remove residual H.sub.2S. The resulting light yellow, viscous sticky oil had a \*\*\*thiol\*\*\* sulfur (titration by modified ASTM D3227) content of 7.53

wt. %, 2.5 SH/molecule, or 2.35 meq SH/g. Combustion analysis indicated C, 64.37%; H, 10.20%; N, <0.15%; and S, 9.51%.

DETD Epoxidized Soybean Oil (600 g, .about.0.6 mol) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 5.0 g, 32.4 mmol) were charged to a 1-L Hastelloy C autoclave reactor, and the vessel was pressure tested to 630 psig. Hydrogen sulfide (H.sub.2S, 204.0 g, 5.99 mol) was then pressured into the stirred reactor contents through a dip tube in the liquid space. The reaction mixture was heated and maintained at 97.degree. C. with stirring for 14 hrs, during which time the reactor pressure decreased from a maximum of 509 psig to 229 psig. The stirrer was stopped and while still warm (90-95.degree. C.), excess H.sub.2S was slowly vented to a low-pressure flare. The reactor vapor space was then swept with N.sub.2 for 1 hr and the reactor contents drained warm (80-85.degree. C.). The reaction product was N.sub.2 sparged under vacuum (<50 mmHg) at 130-140.degree. C. for 16 hrs to remove residual H.sub.2S. The resulting light yellow, viscous sticky oil had a \*\*\*thiol\*\*\* sulfur (titration by modified ASTM D3227) content of 4.14

wt. %, 1.4 SH/molecule, or 1.29 meq SH/g. Combustion analysis indicated C, 65.18%; H, 10.17%; N, <0.15%; and S, 7.80%.

DETD Epoxidized Soybean Oil (600 g, .about.0.6 mol) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 5.0 g, 32.4 mmol) were charged to a 1-L Hastelloy C autoclave reactor, and the vessel was pressure tested to 630 psig. Hydrogen sulfide (H.sub.2S, 204.0 g, 5.99 mol) was then pressured into the stirred reactor contents through a dip tube in the liquid space. The reaction mixture was heated and maintained at 85.degree. C. with stirring for 10 hrs, during which time the reactor pressure decreased from a maximum of 578 psig to 489 psig. The stirrer was stopped and while still warm (80-85.degree. C.), excess H.sub.2S was slowly vented to a low-pressure flare. The reactor vapor space was then swept with N.sub.2 for 1 hr and the reactor contents drained warm (80-85.degree. C.). The reaction product was N.sub.2 sparged under vacuum (<50 mmHg) at 130-140.degree. C. for 16 hrs to remove residual H.sub.2S. The resulting light yellow, viscous sticky oil had a \*\*\*thiol\*\*\* sulfur (titration with modified ASTM D3227) content of 8.28 wt. %, 2.8 SH/molecule, or 2.58 meq SH/g. Combustion analysis indicated C, 65.24%; H, 9.52%; N, 0.18%; and S, 9.53%.

DETD Epoxidized soybean oil (600 g, .about.0.6 mol) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 5.0 g, 32.4 mmol) were charged to a 1-L Hastelloy C autoclave reactor that was pressure tested to 630 psig. Hydrogen sulfide (H.sub.2S, 204.0 g, 5.99 mol) was then pressured into the stirred reactor contents through a dip tube in the liquid space. The reaction mixture was heated and maintained at 85.degree. C. with stirring for 12 hrs, during which time the reactor pressure decreased from a maximum of 587 psig to 498 psig. The stirrer was stopped and while still warm (80-85.degree. C.), excess H.sub.2S was slowly vented to a low-pressure flare. The reactor vapor space was then swept with N.sub.2 for 1 hr and the reactor contents drained warm (80-85.degree. C.). The reaction product was N.sub.2 sparged under vacuum (<50 mmHg) at 130-140.degree. C. for 16 hrs to remove residual H.sub.2S. The resulting light yellow, viscous sticky oil had a \*\*\*thiol\*\*\* sulfur (titration by modified ASTM D3227) content of 8.24 wt. %, 2.8 SH/molecule, or 2.57 meq SH/g. Combustion analysis indicated

C, 63.39%; H, 10.01%; N, <0.15%; and S, 8.76%.

DETD Epoxidized soybean oil (600 g, .about.0.6 mol) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 5.0 g, 32.4 mmol) were charged to a 1-L Hastelloy C autoclave reactor, and the vessel was pressure tested to 630 psig. Hydrogen sulfide (H.sub.2S, 204.0 g, 5.99 mol) was then pressured into the stirred reactor contents through a dip tube in the liquid space. The reaction mixture was heated and maintained at 85.degree. C. with stirring for 8 hrs, during which time the reactor pressure decreased from a maximum of 606 psig to 537 psig. The stirrer was stopped and while still warm (80-85.degree. C.), excess H.sub.2S was slowly vented to a low-pressure flare. The reactor vapor space was then swept with N.sub.2 for 1 hr and the reactor contents drained warm (80-85.degree. C.). The reaction product was N.sub.2 sparged under vacuum (<50 mmHg) at 130-140.degree. C. for 16 hrs to remove residual H.sub.2S. The resulting light yellow, viscous sticky oil had a \*\*\*\*thiol\*\*\* sulfur (titration by modified ASTM D3227) content of 7.34 wt. %, 2.5 SH/molecule, or 2.29 meq SH/g. Combustion analysis indicated C, 64.47%; H, 10.18%; N, <0.15%; and S, 8.40%.

DETD Epoxidized soybean oil (600 g, .about.0.6 mol) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 5.0 g, 32.4 mmol) were charged to a 1-L Hastelloy C autoclave reactor that was pressure tested to 630 psig. Hydrogen sulfide (H.sub.2S, 204.0 g, 5.99 mol) was then pressured into the stirred reactor contents through a dip tube in the liquid space. The reaction mixture was heated and maintained at 85.degree. C. with stirring for 6 hrs, during which time the reactor pressure decreased from a maximum of 586 psig to 556 psig. The stirrer was stopped and while still warm (80-85.degree. C.), excess H.sub.2S was slowly vented to a low-pressure flare. The reactor vapor space was then swept with N.sub.2 for 1 hr and the reactor contents drained warm (80-85.degree. C.). The reaction product was N.sub.2 sparged under vacuum (<50 mmHg) at 130-140.degree. C. for 16 hrs to remove residual H.sub.2S. The resulting light yellow, viscous sticky oil had a \*\*\*\*thiol\*\*\* sulfur (titration by modified ASTM D3227) content of 5.93 wt. %, 2.0 SH/molecule, or 1.85 meq SH/g. Combustion analysis indicated C, 65.26%; H, 10.19%; N, <0.15%; and S, 8.43%.

DETD Epoxidized soybean oil (600 g, .about.0.6 mol) and

1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 5.0 g, 32.4 mmol) were charged to a 1-L Hastelloy C autoclave reactor, and the vessel was pressure tested to 630 psig. Hydrogen sulfide (H.sub.2S, 204.0 g, 5.99 mol) was then pressured into the stirred reactor contents through a dip tube in the liquid space. The reaction mixture was heated and maintained at 85.degree. C. with stirring for 4 hrs, during which time the reactor pressure decreased from a maximum of 595 psig to 554 psig. The stirrer was stopped and while still warm (80-85.degree. C.), excess H.sub.2S was slowly vented to a low-pressure flare. The reactor vapor space was then swept with N.sub.2 for 1 hr and the reactor contents drained warm (80-85.degree. C.). The reaction product was N.sub.2 sparged under vacuum (<50 mmHg) at 130-140.degree. C. for 16 hrs to remove residual H.sub.2S. The resulting light yellow, viscous sticky oil had a \*\*\*thiol\*\*\* sulfur (titration by modified ASTM D3227) content of 5.36 wt. %, 1.8 SH/molecule, or 1.67 meq SH/g. Combustion analysis indicated C, 65.67%; H, 10.17%; N, 0.34%; and S, 9.84%.

DETD Epoxidized soybean oil (600 g, .about.0.6 mol) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 5.0 g, 32.4 mmol) were charged to a 1-L Hastelloy C autoclave reactor that was pressure tested to 630 psig. Hydrogen sulfide (H.sub.2S, 204.0 g, 5.99 mol) was then pressured into the stirred reactor contents through a dip tube in the liquid space. The reaction mixture was heated and maintained at 85.degree. C. with stirring for 4 hrs, during which time the reactor pressure decreased from a maximum of 577 psig to 519 psig. The stirrer was stopped and while still warm (80-85.degree. C.), excess H.sub.2S was slowly vented to a low-pressure flare. The reactor vapor space was then swept with N.sub.2 for 1 hr and the reactor contents drained warm (80-85.degree. C.). The reaction product was N.sub.2 sparged under vacuum (<50 mmHg) at 130-140.degree. C. for 16 hrs to remove residual H.sub.2S. The resulting light yellow, viscous sticky oil had a \*\*\*thiol\*\*\* sulfur (titration with AgNO.sub.3) content of 5.85 wt. %, 2.0 SH/molecule, or 1.82 meq SH/g. Combustion analysis indicated C, 65.09%; H, 10.15%; N, 0.35%; and S, 10.63%.

DETD Epoxidized soybean oil (600 g, .about.0.6 mol) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 5.0 g, 32.4 mmol) were charged

to a 1-L Hastelloy C autoclave reactor, and the vessel was pressure tested to 630 psig. Hydrogen sulfide (H.sub.2S, 204.0 g, 5.99 mol) was then pressured into the stirred reactor contents through a dip tube in the liquid space. The reaction mixture was heated and maintained at 85.degree. C. with stirring for 2 hrs, during which time the reactor pressure decreased from a maximum of 577 psig to 508 psig. The stirrer was stopped and while still warm (80-85.degree. C.), excess H.sub.2S was slowly vented to a low-pressure flare. The reactor vapor space was then swept with N.sub.2 for 1 hr and the reactor contents drained warm (80-85.degree. C.). The reaction product was N.sub.2 sparged under vacuum (<5 mmHg) at 130-140.degree. C. for 16 hrs to remove residual H.sub.2S. The resulting light yellow, viscous sticky oil had a \*\*\*thiol\*\*\* sulfur (titration by modified ASTM D3227) content of 5.07 wt. %, 1.7 SH/molecule, or 1.58 meq SH/g. Combustion analysis indicated C, 63.96%; H, 10.01%; N, 0.35%; and S, 11.22%. DETD Table 5 provides the properties of the mercaptohydroxy soybean oil samples produced in Examples 1-10.

TABLE 5

Ex- ***Epoxide*** ample molecule.sup.3 Ratio	Reac- tion Time (hrs)	Reac- tion Temp (.degree. C.)	***Mercaptan***		***Epoxides***	
			Sulfur	SH per	left per	groups
		:SH	(wt. %).1	molecule.1	molecule.2	
		Molar				
		Ratio				
1	0	N/A	N/A	0	4.3	--
2	8	85	7.53	2.5	1.8	0.72
3	14	97	4.14	1.4	2.9	2.07
4	10	85	8.28	2.8	1.5	0.54
5	12	85	8.24	2.8	1.5	0.54
6	8	85	7.34	2.5	1.8	0.72
7	6	85	5.93	2.0	2.3	1.15
8	4	85	5.36	1.8	2.5	1.40
9	4	85	5.85	2.0	2.3	1.15
10	2	85	5.07	1.7	2.6	1.529

.sup.1Thiol sulfur was determined by silver nitrate oxidation using ASTM D 3227

.sup.2Determined by wt. % \*\*\*thiol\*\*\* sulfur

.sup.3Determined by subtracting the SH/molecule from the starting material

\*\*\*epoxide\*\*\* content

DETD Epoxidized soybean oil and the catalyst were charged to a 1-L

Hastelloy

C autoclave reactor, and the vessel was pressure tested to 1000 psig.

Hydrogen sulfide was then pressured into the stirred reactor contents

through a dip tube in the liquid space. The reaction mixture was heated

and maintained at temperature a set period of time with stirring for 12

hrs. During the reaction time the reactor pressure usually decreased. At

the end of the reaction time, the stirrer was stopped and excess H.sub.2S was slowly vented while the reaction mixture was warm to

a

low-pressure flare. The reactor vapor space was then swept with N.sub.2

for 1 hr and the reactor contents drained. The reaction product was

N.sub.2 sparged under vacuum (<50 mmHg) at 100.degree. C. for 16 hrs to

remove residual H.sub.2S. Table 6 provides the reaction conditions used

to produce the mercaptohydroxy soybean oils for several runs and the

\*\*\*thiol\*\*\* sulfur content of the mercaptohydroxy soybean oils

produced.

TABLE 6

#### Mercaptohydroxy Soybean Oil Production Runs

Run (minutes)	Epoxidized Soybean Oil		Catalyst (g)	H.sub.2S ***Thiol*** (g)	H.sub.2S: Sulfur Molar Ratio	***Epoxide*** Sulfur (.degree. C.)
	Temperature (g)	Time (g)				
	(wt. %)					
556-41.sup..dagger. 728	249.6 5.69		1.950	214.0	5.86	64
556-53.sup..dagger. 370	250.0 9.04		2.000	213.0	5.81	100
556-47.sup..dagger. 720	250.5 10.47		1.050	213.0	5.81	101
407-81D.sup..dagger. 480	500.0 7.53		4.200	255.0	3.49	85
407-86.sup..dagger. 600	600.0 8.28		5.000	204.0	2.07	85
556-79.sup..dagger-dbl. 720	250.0 6.68		2.600	214.0	5.83	100
556-80.sup..dagger-dbl. 720	251.0 9.51		5.000	214.0	5.81	100

.sup..dagger.Catalyst was DBU

.sup..dagger-dbl.catalyst was triethylamine (TEA)

.sup.aThiol sulfur measured by silver nitrate titration using modified ASTM D

3227

DETD Run number 407-86 was subjected to the sodium methoxide methanolysis

procedure and subsequently analyzed by GC/MS. The GC/MS analysis indicated that the product had \*\*\*epoxide\*\*\* group to  
\*\*\*thiol\*\*\*  
group molar ratio of approximately 0.14. The methanolysis data also indicated that an average of 80.4 percent of the product mercaptohydroxy soybean oil contained sulfur.

DETD Mercaptanized soybean oil (900.1 g; 10.92 wt. % \*\*\*thiol\*\*\* sulfur,) was charged to a three necked flask along with elemental sulfur pellets (9.6 g). The reaction mixture was heated to 120.degree. C. until sulfur dissolved and then cooled to 99.degree. C. Tributylamine (4.8 g) was charged to the reaction mixture with an addition funnel drop wise. The reaction mixture was mixed at 90.degree. C. for 2 hrs. H.sub.2S evolution was observed. The reaction product (904.8 g) was sparged with N.sub.2 under vacuum at 110.degree. C. for 4 hrs to remove residual H.sub.2S. The final product was a light yellow oil with a \*\*\*thiol\*\*\* sulfur of 6.33 wt. % (by modified ASTM D3227). The elemental combustion analysis was 70.19%; C, 10.37%; H, and 11.21%; S.

DETD Mercaptanized soybean oil (900.0 g; 10.92 wt. % \*\*\*thiol\*\*\* sulfur,) was charged to a three necked flask along with elemental sulfur pellets (36.0 g). The reaction mixture was heated to 120.degree. C. until sulfur dissolved and then cooled to 100.degree. C. Tributylamine (4.8 g) was charged to the reaction mixture with an addition funnel drop wise. The reaction mixture was mixed at 90.degree. C. for 36 hrs. H.sub.2S evolution was observed. The reaction product (825.6 g) was sparged with N.sub.2 under vacuum at 90.degree. C. for 36 hrs to remove residual H.sub.2S. The reaction product was then sparged with N.sub.2 under vacuum at 110.degree. C. for 3 hrs to remove residual H.sub.2S. The final product was a light yellow oil with a \*\*\*thiol\*\*\* sulfur of 2.36 wt. % (by modified ASTM D3227). The elemental combustion analysis was 68.90%; C, 11.07%; H, and 12.25%; S.

DETD Mercaptanized soybean oil (900.1 g; 10.92 wt. % \*\*\*thiol\*\*\* sulfur,) was charged to a three necked flask along with elemental sulfur pellets (18.0 g). The reaction mixture was heated to 125.degree. C. until sulfur dissolved and then cooled to 101.degree. C. Tributylamine (4.8 g) was charged to the reaction mixture with an addition funnel drop wise. The reaction mixture was mixed at 90.degree. C. for 2 hrs.



H.sub.2S evolution was observed. The reaction product (901.5 g) was sparged with N.sub.2 under vacuum at 110.degree. C. for 4 hrs to remove residual H.sub.2S. The final product was a light yellow oil with a  
 \*\*\*thiol\*\*\* sulfur of 4.9 wt. % (by modified ASTM D3227). The elemental combustion analysis was 69.58%; C, 11.25%; H, and 11.31%; S.

DETD Mercaptanized soybean oil (900.2 g; 10.92 wt. % \*\*\*thiol\*\*\* sulfur,) was charged to a three necked flask along with elemental sulfur pellets (45.0 g). The reaction mixture was heated to 125.degree. C. until sulfur dissolved and then cooled to 100.degree. C. Tributylamine (4.8 g) was charged to the reaction mixture with an addition funnel drop wise. The reaction mixture was mixed at 90.degree. C. for 2 hrs. H.sub.2S evolution was observed. The reaction product (915.0 g) was sparged with N.sub.2 under vacuum at 110.degree. C. for 4 hrs to remove residual H.sub.2S. The final product was a light yellow oil with a  
 \*\*\*thiol\*\*\* sulfur of 1.41 wt. % (by modified ASTM D3227). The elemental combustion analysis was 68.35%; C, 10.98%; H, and 13.28%; S.

DETD Numerous polythiourethane compositions were prepared by reacting a  
 \*\*\*thiol\*\*\* ester composition with a diisocyanate in the presence of a catalyst by using the processes described herein for preparing such polythiourethane compositions. The compositions were produced using the different variables of feedstocks, diisocyanates, stoichiometry, and catalysts shown in Table 8. Once every combination of variable was used, over 1200 compositions were produced. Each of the feedstocks were reacted with each of the diisocyanates at each of the stoichiometries with each of the catalysts listed to produce the 1200+ compositions. The stoichiometry was based upon a \*\*\*thiol\*\*\* ester composition (MSO, MHSO, CMSO, MCO) active hydrogen ( \*\*\*thiol\*\*\* and hydroxyl group) to diisocyanate equivalent ratio. For example, castor oil was reacted with toluene diisocyanate at a stoichiometric value of 1.25 while using Jeffol.RTM. A-480 as the catalyst. As another example, a  
 \*\*\*thiol\*\*\* ester composition was reacted with methane diisocyanate at a stoichiometric value of 0.9 while using the DABCO catalyst.

DETD In the first MCO polythiourethane example, MCO was weighed into a

polyethylene beaker. To the MCO agent was added Luprinate at a  
 \*\*\*thiol\*\*\* to isocyanate mole ratio of 0.95. To this  
 reaction mixture  
 was added dibutyl tin dilaurate (DBTDL) at a weight percent of  
 0.125  
 based upon the total weight of the ingredients. The three-  
 component  
 reaction mixture was then manually stirred with a wooden Popsicle  
 stick.  
 The entire pre-polymer mixture was then poured into a mold for  
 curing  
 and cured using curing profile B. After the curing time was  
 complete it  
 was determined that the preparation produced a polythiourethane  
 polymer.  
 DETD In the second MCO polythiourethane example, MCO was weighed into  
 a  
 polyethylene beaker. To the MCO agent was added Luprinate M20S at  
 a  
 \*\*\*thiol\*\*\* to isocyanate mole ratio of 1.00. To this  
 reaction mixture  
 was added dibutyl tin dilaurate (DBTDL) at a weight percent of  
 0.125  
 based upon the total weight of the ingredients. The three-  
 component  
 reaction mixture was then manually stirred with a wooden Popsicle  
 stick.  
 The entire pre-polymer mixture was then poured into a mold for  
 curing  
 and cured using curing profile B. After the curing time was  
 complete it  
 was determined that the preparation produced a polythiourethane  
 polymer.  
 DETD In the polythiourethane compositions, the feedstock  
 \*\*\*thiol\*\*\*  
 ester compositions that were used included MSO (mercaptanized  
 soybean  
 oil), MHSO (mercaptohydroxy soybean oil), CMSO (cross-linked  
 mercaptanized soybean oil), castor oil, and MCO (mercaptanized  
 castor  
 oil). The diisocyanates that were used to produce these  
 compositions  
 included MDI (4,4'-methylenebis(phenyl) diisocyanate), HMDI  
 (4,4'-methylenebis(cyclohexyl) diisocyanate, which is also known  
 as  
 hydrogenated MDI), TDI (tolylene 2,4-diisocyanate), HDI  
 (1,6-diisocyanatohexane, which is also known as hexamethylene  
 diisocyanate), and Luprinate.TM. M20S (which is an oligomerized  
 form of  
 MDI and is also referred to as polymeric MDI that is produced by  
 BASF  
 Corporation). The catalysts that were used included DABCO  
 (diazabicyclooctane-di-tertiary amine), DBTDL (dibutyl tin  
 dilaurate-organometallic catalyst), Jeffol.RTM. A-480 (which is a  
 tertiary amine polyol produced by Huntsman Based Chemicals), and  
 BDMA  
 (benzyl dimethylamine).  
 DETD B1: Mercaptanized soybean oil (an example of MVO discussed  
 above)--Polymercaptan 358, available from Chevron Phillips  
 Chemical Co.;

8.65% \*\*\*thiol\*\*\* sulfur; 370 equivalent weight; viscosity of 510.6 cSt @ 21.degree. C.;

DETD B2: Mercapto-hydroxy soybean oil (an examples of MHVO discussed above)--A mercapto-hydroxy soybean oil made by the free radical addition of hydrogen sulfide to epoxidized soybean oil; the mercapto and hydroxy functionalities are equal; 8.335% \*\*\*thiol\*\*\* sulfur; equivalent weight 192 (including both mercapto and hydroxy functionalities);

DETD B3: Sulfur cross-linked mercaptanized soybean oil (an example of CMVO discussed above)--A sulfur cross-linked mercaptanized soybean oil made by the addition of elemental sulfur to mercaptanized soybean oil; \*\*\*thiol\*\*\* sulfur content 6.33%; equivalent weight 506;

DETD B4: Sulfur cross-linked mercaptanized soybean oil (an example of CMVO discussed above)--A sulfur cross-linked mercaptanized soybean oil made by the addition of elemental sulfur to mercaptanized soybean oil; \*\*\*thiol\*\*\* sulfur content 7.64%; equivalent weight 419; cross-linkcross-link

DETD F2: Amine catalyst: 1,8-Diazabicyclo[5,4,0]undec-7-ene (DBU), CAS# \*\*\*6674-22-2\*\*\* .

DETD Analysis of the \*\*\*Thiol\*\*\* Containing Esters, Hydroxy \*\*\*Thiol\*\*\* Containing Esters and Cross-Linked \*\*\*Thiol\*\*\* Containing Ester

DETD Particular aspects of the \*\*\*thiol\*\*\* containing esters, hydroxy \*\*\*thiol\*\*\* containing esters, cross-linked \*\*\*thiol\*\*\* ester, unsaturated esters and epoxidized unsaturated esters are measured particular analytical techniques. \*\*\*Thiol\*\*\* sulfur values were obtained using a silver nitrate titration as described in ASTM D3227 or by Raman spectroscopy. Carbon-carbon double bond to \*\*\*thiol\*\*\* group molar ratio, cyclic sulfide to \*\*\*thiol\*\*\* group molar ratios were determined by .sup.13C NMR and/or GC analysis of the \*\*\*thiol\*\*\* containing ester or hydroxy \*\*\*thiol\*\*\* containing ester side chains.

DETD \*\*\*Thiol\*\*\* Sulfur Content by Raman Spectroscopy

DETD \*\*\*Thiol\*\*\* sulfur content was measured by both silver nitrate titration, ASTM D3227, and/or Raman spectroscopy. The Raman spectroscopy method is practiced by measuring the Raman spectra of the \*\*\*thiol\*\*\* containing ester, hydroxy \*\*\*thiol\*\*\* containing ester, cross-linked \*\*\*thiol\*\*\* ester and comparing the spectra to calibration standards containing know \*\*\*thiol\*\*\* compounds having know amounts of \*\*\*thiol\*\*\* groups. Generally, the calibration standard \*\*\*thiol\*\*\*

compound has a similar structure to the \*\*\*thiol\*\*\* containing esters analyzed.

DETD The \*\*\*thiol\*\*\* containing esters, hydroxy \*\*\*thiol\*\*\* containing esters and cross-linked \*\*\*thiol\*\*\* ester \*\*\*thiol\*\*\* content were determined by comparing the Raman spectra of the \*\*\*thiol\*\*\* containing esters, hydroxy \*\*\*thiol\*\*\* containing esters and cross-linked \*\*\*thiol\*\*\* ester to calibration standards prepared from mercaptanized methyl oleate diluted in soybean oil to known \*\*\*thiol\*\*\* sulfur contents. \*\*\*Thiol\*\*\* sulfur calibration standards were prepared using standards using various known concentration of mercaptanized methyl oleate diluted in soybean oil.

DETD Raman spectra of the calibration standards and the \*\*\*thiol\*\*\* containing esters, hydroxy \*\*\*thiol\*\*\* containing esters and cross-linked \*\*\*thiol\*\*\* ester were measured using a Kaiser Hololab 5000 Process Raman spectrometer, using a 785 nm laser.

\*\*\*Thiol\*\*\* containing esters, hydroxy \*\*\*thiol\*\*\* containing esters and cross-linked \*\*\*thiol\*\*\* ester samples and the \*\*\*thiol\*\*\* sulfur calibration standard Raman spectra were obtained by collecting four 10 second scans which were then processed using Holoreact software.

\*\*\*Thiol\*\*\* sulfur values for the \*\*\*thiol\*\*\* containing esters, hydroxy \*\*\*thiol\*\*\* containing esters and cross-linked \*\*\*thiol\*\*\* ester were then calculated using the ratio of the peak area values of the \*\*\*thiol\*\*\* SH peak (center: 2575 cm<sup>-1</sup>; area 2500-2650 cm<sup>-1</sup>), and the C.dbd.O peak (center--1745 cm<sup>-1</sup>; area--1700-1800 cm<sup>-1</sup>) and comparing them to the peak area values for the calibration standards and interpolating the containing esters, hydroxy \*\*\*thiol\*\*\* containing esters and cross-linked \*\*\*thiol\*\*\* ester \*\*\*thiol\*\*\* sulfur contents. Repeatability of the \*\*\*thiol\*\*\* sulfur values as measured by Raman spectroscopy have been shown to have a standard deviation of 0.05-0.1 and a % RSD of 0.6-1.5 using 5 samples having a % \*\*\*thiol\*\*\* sulfur content ranging from 3.1-10.6 weight percent as measured over a two month period.

DETD The Raman spectroscopy technique for determining the \*\*\*thiol\*\*\* sulfur content of a \*\*\*thiol\*\*\* containing ester, hydroxy \*\*\*thiol\*\*\* containing ester, and a cross-linked \*\*\*thiol\*\*\*

containing ester has been illustrated using a \*\*\*thiol\*\*\* containing ester produced from soybean oil. However, one skilled in the art may adapt and apply the Raman spectroscopy technique for determining the \*\*\*thiol\*\*\* sulfur content of other \*\*\*thiol\*\*\* containing esters, hydroxy \*\*\*thiol\*\*\* containing esters, and a cross-linked \*\*\*thiol\*\*\* containing esters described herein.

DETD C.dbd.C to \*\*\*Thiol\*\*\* Group and Cyclic Sulfide Group to \*\*\*Thiol\*\*\* Group Molar Ratios by .sup.13C NMR

DETD Carbon-carbon double bond to \*\*\*thiol\*\*\* group molar ratio and cyclic sulfide group to \*\*\*thiol\*\*\* group molar ratios were determined by .sup.13C NMR. \*\*\*Thiol\*\*\* containing ester .sup.13C NMR spectra were obtained on a Varian Mercury INOVA400 NMR, a Varian Mercury Plus 300 NMR, or equivalent spectrometer (75.5 MHz .sup.13C NMR). Peak areas were determined for the cyclic sulfide carbon atoms, \*\*\*thiol\*\*\* group HS--C carbon atoms and carbon-carbon double bonds carbon atoms using the .sup.13C NMR regions indicated in the table below:

Functional Group	.sup.13C NMR Region	Number of Carbon Atoms/Group
Cyclic Sulfide Carbon Atoms	49-49.5 ppm	2
HS--C Carbon Atoms	40-41.5 ppm	1
C.dbd.C Carbon Atoms	120-140 ppm	2
DETD The ***thiol*** containing ester cyclic sulfide to ***thiol*** group molar ratio were calculated by dividing the cyclic sulfide carbon atoms .sup.13C NMR peak area by 2 (to account for the 2 carbon atoms per cyclic sulfide group) and dividing the resultant number by the ***thiol*** group HS--C carbon atoms .sup.13C NMR peak area.		
The ***thiol*** containing ester carbon-carbon double bond to ***thiol*** group molar ratio were calculated by dividing the C.dbd.C carbon atoms .sup.13C NMR peak area by 2 (to account for the 2 carbon atoms per carbon-carbon double bond) and dividing the result number by the ***thiol*** group HS--C carbon atoms .sup.13C NMR peak area		
Offset sample .sup.13C NMR's for soybean oil and a ***thiol*** containing ester produced from soybean oil using the disclosed process is provided as FIG. 1.		
DETD The NMR technique for analyzing the unsaturated ester and the		

\*\*\*thiol\*\*\* containing ester produced from an unsaturated ester have been illustrated using <sup>13</sup>C NMR on soybean oil the \*\*\*thiol\*\*\* containing ester produced from soybean oil. However, one skilled in the art may adapt and apply either the <sup>13</sup>C NMR or <sup>1</sup>H NMR technique to analyze the unsaturated esters and \*\*\*thiol\*\*\* containing ester produced from the unsaturated ester described herein.

DETD \*\*\*Epoxide\*\*\* Group to \*\*\*Thiol\*\*\* Group Molar Ratios by <sup>13</sup>C or <sup>1</sup>H NMR

DETD The \*\*\*epoxide\*\*\* group to \*\*\*thiol\*\*\* group molar ratios were determined using <sup>1</sup>H or <sup>13</sup>C NMR. Hydroxy \*\*\*thiol\*\*\* containing ester <sup>1</sup>H or <sup>13</sup>C NMR spectra were obtained on a Varian Mercury INOVA400 NMR, a Varian Mercury Plus 300 NMR, or equivalent spectrometer (300 MHz <sup>1</sup>H NMR--75.5 MHz <sup>13</sup>C NMR).

Peak areas were determined for the \*\*\*epoxide\*\*\* group and sulfide group using the <sup>13</sup>C and or <sup>1</sup>H regions indicated in the table below:

Functional Group	<sup>1</sup> H NMR Region	<sup>13</sup> C NMR Region	Number of Carbon Atoms/Group	Number of Hydrogen Atoms/Group
***Epoxide***	2.75-3.2	ppm	53.6-56.6	ppm 2
2 Group Carbon Atoms				
HS--C Carbon Atoms	3.2-4	ppm	40-41.5	ppm 1
DETD	The hydroxy ***thiol*** containing ester ***epoxide*** group to ***thiol*** group molar ratio were calculated by dividing the ***epoxide*** group carbon atoms <sup>1</sup> H NMR peak area by 2 (to account for the 2 hydrogen atoms attached to the ***epoxide*** carbon atoms) and dividing the result number by the ***thiol*** group HS--C carbon atom hydrogens <sup>13</sup> C NMR peak area. Similarly, hydroxy ***thiol*** containing ester ***epoxide*** group to ***thiol*** group molar ratio were calculated using <sup>13</sup> H NMR areas.			
DETD	The average number of ***epoxide*** group per epoxidized unsaturated ester molecule can be determined utilizing similar			

methods  
utilizing either the carbonyl group carbon atom or the C--O ester  
group  
carbon atoms <sup>13</sup>C NMR peak areas in conjunction with the  
\*\*\*epoxide\*\*\* group <sup>13</sup>C NMR peak area. Sample <sup>1</sup>H  
NMR's  
epoxidized soybean oil and a \*\*\*thiol\*\*\* containing ester  
produced  
from epoxidized soybean oil 1 are provided in FIG. 2.  
DETD The NMR technique for analyzing the epoxidized unsaturated ester  
and  
the \*\*\*thiol\*\*\* containing ester produced from an epoxidized  
unsaturated ester (a hydroxy \*\*\*thiol\*\*\* containing ester)  
has been  
illustrated using <sup>1</sup>H NMR on epoxidized soybean oil the  
\*\*\*thiol\*\*\* containing ester produced from epoxidized soybean  
oil.  
However, one skilled in the art may adapt and apply either the  
<sup>1</sup>H  
NMR or <sup>13</sup>C NMR technique to analyze the epoxidized  
unsaturated  
esters and \*\*\*thiol\*\*\* containing ester produced from the  
epoxidized  
unsaturated ester described herein.  
DETD Analysis of Unsaturated Esters, Epoxidized Unsaturated Esters,  
\*\*\*Thiol\*\*\* Containing Esters, and Hydroxy \*\*\*Thiol\*\*\*  
Containing  
Esters by Methanolysis  
DETD Many properties of the unsaturated esters, epoxidized  
unsaturated  
esters, \*\*\*thiol\*\*\* containing esters, and hydroxy  
\*\*\*thiol\*\*\*  
containing ester were and/or can be determined by converting the  
complex  
ester molecules into their component polyols and carboxylic acid  
methyl  
esters. The converted esters are then analyzed by gas  
chromatography  
(GC) and/or gas chromatography/mass spectrometry (GCMS) to  
determine the  
composition of the complex ester side chains. Properties that are  
or can  
be determined by the methanolysis followed by GC or GC/MS of the  
carboxylic acid methyl esters include the number of side chain  
that  
contain \*\*\*thiol\*\*\* groups, the percent of \*\*\*thiol\*\*\*  
group  
sulfur, the number of (or average number) of double bonds per  
ester  
molecule, the molecular weight distribution (or average molecular  
weight) of the ester side chains, the number of (or average  
number of)  
\*\*\*epoxide\*\*\* groups per ester molecule, the cyclic sulfide  
to  
\*\*\*thiol\*\*\* group molar ratio, the carbon-carbon double bond  
to  
\*\*\*thiol\*\*\* group molar ratio, and the \*\*\*epoxide\*\*\*  
group to  
\*\*\*thiol\*\*\* group molar ratio, among others.  
DETD Depending upon the material being subjected to the methanolysis

procedure, there are two methanolysis procedures that were practiced upon the unsaturated ester, epoxidized esters, \*\*\*thiol\*\*\* containing ester, and hydroxy \*\*\*thiol\*\*\* containing esters described within the experimental section.

DETD Unsaturated esters and \*\*\*thiol\*\*\* containing ester produced from unsaturated ester were subjected to a hydrogen chloride based methanolysis procedure. In the hydrogen chloride methanolysis procedure, a 50 to 100 mg sample of the \*\*\*thiol\*\*\* containing ester is contacted with 3 mL of 3 N methanolic HCl and reacted for 2 hours a 50.degree. C. The solution is then allowed to cool and the neutralized with a dilute sodium bicarbonate solution. The solution's organic components are then extracted with ethyl ether and analyzed by GC and/or GC/MS. Additional details for the methanolic hydrogen chloride methanolysis procedure may be found in the product specification sheet for methanolic HCl, 0.5 N and 3 N as supplied by Supelco.

DETD Epoxidized unsaturated esters and hydroxy \*\*\*thiol\*\*\* containing esters produced from epoxidized unsaturated esters were subjected to a sodium methoxide based methanolysis procedure. The sodium methoxide methanolysis procedure was based upon the procedure disclosed in U.S. Pat. No. 3,991,089. In the sodium methoxide methanolysis procedure, approximately 1 g of the ester was placed in a 50 mL vial with 5.0 mL 25% sodium methoxide in methanol, and 10 mL methanol. The mixture was shaken for approximately 1 hour at room temperature, during which time the solution became one phase. The mixture was then poured into 25 mL of distilled water. Diethyl ether, 25 mL, was added to the solution and the mixture was acidified with 0.5 N HCL to a pH of approximately 5. The organic layer was separated from the aqueous layer using a separatory funnel. The organic layer was washed successively with distilled water (15 mL) and brine solution (15 mL) and then dried over magnesium sulfate. The magnesium sulfate was separated from the organic solution by filtration and the solvent removed by rotary evaporation.

DETD FIG. 3 provides a GC/MS trace of a mercaptanized soybean oil subjected to the methanolysis procedure and analyzed by GC/MS using a HP-5 30 m.times.0.32 mm id.times.0.25 .mu.m film thickness GC Column. Table 11 provides the GC/MS trace peak assignments.

TABLE 11



GC/MS Data for Methanolysis of A \*\*\*Thiol\*\*\* Containing Ester  
 Produced from  
 Soybean Oil

GC Retention time                      Methyl Ester Carboxylic Acid Assignment

21.58	Methyl hexadecanoate
23.66	Methyl (C18 monoene)oate
23.74	Methyl (C18 monoene)oate
23.96	Methyl octadecanoate
26.46	Methyl (C18 Monoene monomercaptan)oate
26.59	Methyl (C18 Monoene monomercaptan)oate
26.66	Methyl (C18 Monoene monomercaptan)oate
26.80	Methyl (C18 monomercaptan)oate
27.31	Methyl (C18 cyclic sulfide)oate
27.44	Methyl (C18 cyclic sulfide)oate
29.04	Methyl (C18 dimercaptan)oate
29.15	Methyl (C18 dimercaptan)oate
29.37	Methyl (C18 monoene dimercaptan)oate
29.46	Methyl (C18 monoene dimercaptan)oate
30.50	Methyl (C18 di (cyclic sulfide))oate

Peaks at 29.37 or 29.46 could also contain Methyl (C18 cyclic sulfide monomercaptan)oate isomers as part of those peaks.

DETD    FIG. 5 provides a GC/MS trace of an epoxidized soybean oil contacted

with hydrogen sulfide (a hydroxy \*\*\*thiol\*\*\* containing ester)

subjected to the methanolysis procedure and analyzed by GC/MS using a

HP-5 30 m.times.0.32 mm id.times.0.25 .mu.m film thickness GC Column.

Table 13 provides the GC/MS trace peak assignments.

TABLE 13

GC/MS Data for Methanolysis of a Hydroxy \*\*\*Thiol\*\*\* Containing Ester Produced from Epoxidized Soybean Oil

GC Retention time                      Methyl Ester Carboxylic Acid Assignment

16.09	Methyl hexadecanoate
17.68	Methyl octadecanoate
18.94	Methyl (C18 monoepoxide)oate
19.94	Methyl (C18 diepoxide)oate
20.14	Methyl (C18 diepoxide)oate
20.75	Methyl (C18 monohydroxy monothiol)oate
21-21.5	Methyl (C18 triepoxide)oate
22.82	Methyl (C18 dihydroxy dithiol)oate
22.90	Methyl (C18 monoepoxide monohydroxy monothiol)oate
27-27.5	Unidentified mixture of C18 sulfur containing methyl esters

DETD    The methanolysis procedure and GC/MS procedure has been illustrate

using soybean oil, epoxidized soybean oil, and the \*\*\*thiol\*\*\* containing products derived from soybean oil and epoxidized soybean oil.

However, one skilled in the art can easily adapt the procedures to the

analysis of other unsaturated esters, epoxidized unsaturated ester, and the \*\*\*thiol\*\*\* containing products derived from the unsaturated esters and epoxidized unsaturated esters as described herein.

DETD The polythiourethane produced from the \*\*\*thiol\*\*\* containing esters, hydroxy \*\*\*thiol\*\*\* containing esters, and cross linked \*\*\*thiol\*\*\* containing ester were analyzed using ASTM E1545-95A and E228-95 to provide the glass transition temperatures and the coefficients of thermal expansion. Shore hardness of the polythiourethanes were determined using ASTM D2240-02A. The polythiourethane were also subject to a subjective analysis classifying the polythiourethanes as hard, flexible, rubbery, rigid, tough, brittle, and other characteristics.

CLM What is claimed is:

1. A hydroxy \*\*\*thiol\*\*\* ester composition comprising hydroxy \*\*\*thiol\*\*\* ester molecules having an average of at least 1 ester groups per hydroxy \*\*\*thiol\*\*\* ester molecule and having an average of at least 1 .alpha.-hydroxy \*\*\*thiol\*\*\* groups per hydroxy \*\*\*thiol\*\*\* ester molecule.

CLM What is claimed is:

2. The composition of claim 1, wherein the hydroxy \*\*\*thiol\*\*\* ester molecules have an average ranging from 1.5 to 9 .alpha.-hydroxy \*\*\*thiol\*\*\* groups per hydroxy \*\*\*thiol\*\*\* ester molecule.

CLM What is claimed is:

3. The composition of claim 1, wherein the hydroxy \*\*\*thiol\*\*\* ester molecules have an average of greater than 2.5 weight percent \*\*\*thiol\*\*\* sulfur.

CLM What is claimed is:

4. The composition of claim 1, wherein the hydroxy \*\*\*thiol\*\*\* ester molecules have an average ranging from 8 to 10 weight percent \*\*\*thiol\*\*\* sulfur.

CLM What is claimed is:

5. The composition of claim 1, wherein the hydroxy \*\*\*thiol\*\*\* ester molecules have a molar ratio of \*\*\*epoxide\*\*\* groups to the .alpha.-hydroxy \*\*\*thiol\*\*\* groups of less than 2.

CLM What is claimed is:

6. The composition of claim 1, wherein greater than 40 percent of the hydroxy \*\*\*thiol\*\*\* ester molecule total side chains contain sulfur.

CLM What is claimed is:

7. The composition of claim 1, wherein the composition is substantially free of \*\*\*epoxide\*\*\* groups.

CLM What is claimed is:  
8. A hydroxy \*\*\*thiol\*\*\* ester composition comprising hydroxy \*\*\*thiol\*\*\* ester molecules having an average of at least 1 ester groups per hydroxy \*\*\*thiol\*\*\* ester molecule, having an average of at least 1 \*\*\*thiol\*\*\* groups per hydroxy \*\*\*thiol\*\*\* ester molecule, and having an average of at least 1 alcohol groups per hydroxy \*\*\*thiol\*\*\* ester molecule.

CLM What is claimed is:  
9. The composition of claim 8, wherein the hydroxy \*\*\*thiol\*\*\* ester molecules have an average ranging from 1.5 to 9 \*\*\*thiol\*\*\* groups per hydroxy \*\*\*thiol\*\*\* ester molecule.

CLM What is claimed is:  
10. The composition of claim 8, wherein the hydroxy \*\*\*thiol\*\*\* ester molecules have an average ranging from 1.5 to 9 alcohol groups per hydroxy \*\*\*thiol\*\*\* ester molecule.

CLM What is claimed is:  
11. The composition of claim 8, wherein the hydroxy \*\*\*thiol\*\*\* ester molecules have an average of greater than 2.5 weight percent \*\*\*thiol\*\*\* sulfur.

CLM What is claimed is:  
12. The composition of claim 8, wherein the hydroxy \*\*\*thiol\*\*\* ester molecules have an average ranging from 8 to 10 weight percent \*\*\*thiol\*\*\* sulfur.

CLM What is claimed is:  
13. The composition of claim 8, wherein the hydroxy \*\*\*thiol\*\*\* ester molecules have a molar ratio of \*\*\*epoxide\*\*\* groups to \*\*\*thiol\*\*\* groups of less than 2.

CLM What is claimed is:  
14. The composition of claim 8, wherein greater than 40 percent of the hydroxy \*\*\*thiol\*\*\* ester molecule total side chains contain sulfur.

CLM What is claimed is:  
15. The composition of claim 8, wherein the composition is substantially free of \*\*\*epoxide\*\*\* groups.

CLM What is claimed is:  
16. A process for preparing a hydroxy \*\*\*thiol\*\*\* ester composition,

comprising the steps of: a) contacting hydrogen sulfide and an epoxidized unsaturated ester composition comprising epoxidized unsaturated esters having an average of at least 1 ester groups per epoxidized unsaturated ester molecule and having an average of at least 1 \*\*\*epoxide\*\*\* groups per epoxidized unsaturated ester molecule;  
and b) reacting the hydrogen sulfide and the epoxidized unsaturated esters to form the hydroxy \*\*\*thiol\*\*\* ester composition.

CLM What is claimed is:  
19. The process of claim 16, wherein a molar ratio of the hydrogen sulfide to \*\*\*epoxide\*\*\* groups in the epoxidized unsaturated esters is greater than 1.

CLM What is claimed is:  
21. The process of claim 16, wherein the hydroxy \*\*\*thiol\*\*\* ester composition comprises hydroxy \*\*\*thiol\*\*\* ester molecules having an average of greater than 2.5 weight percent \*\*\*thiol\*\*\* sulfur.

CLM What is claimed is:  
22. The process of claim 16, wherein the hydroxy \*\*\*thiol\*\*\* ester composition comprises hydroxy \*\*\*thiol\*\*\* ester molecules having an average ranging from 8 to 10 weight percent \*\*\*thiol\*\*\* sulfur.

CLM What is claimed is:  
23. The process of claim 16, wherein the hydroxy \*\*\*thiol\*\*\* ester composition comprises hydroxy \*\*\*thiol\*\*\* ester molecules having greater than 40 percent of the hydroxy \*\*\*thiol\*\*\* ester molecule total side chains contain sulfur.

CLM What is claimed is:  
24. A process for preparing a hydroxy \*\*\*thiol\*\*\* ester composition comprising the steps of: a) contacting a polyol composition and a hydroxy \*\*\*thiol\*\*\* carboxylic acid composition; and b) reacting the polyol composition and the hydroxy \*\*\*thiol\*\*\* carboxylic acid composition to produce the hydroxy \*\*\*thiol\*\*\* ester composition comprising hydroxy \*\*\*thiol\*\*\* ester molecules having an average of at least 1 ester groups per hydroxy \*\*\*thiol\*\*\* ester molecule and having an average of at least 1 .alpha.-hydroxy \*\*\*thiol\*\*\*

groups  
per hydroxy \*\*\*thiol\*\*\* ester molecule.

IT 102-85-2, Tri-n-butylphosphite \*\*\*6674-22-2\*\*\* ,  
1,8-Diazabicyclo[5.4.0]undec-7-ene  
(activator; thiol ester compns. prepd. by reacting H2S with  
unsatd.  
esters, such as soybean oil for manuf. monomers for prodn. of  
polythiourethanes for fertilizers)  
ACCESSION NUMBER: 2006:41458 USPATFULL <<LOGINID::20090306>>  
TITLE: \*\*\*Thiol\*\*\* ester compositions and processes  
for  
making and using same  
INVENTOR(S): Brown, Chad W., Bartlesville, OK, UNITED STATES  
Refvik, Mitchell D., Bartlesville, OK, UNITED  
STATES  
Herron, Steven J., Kingwood, TX, UNITED STATES  
PATENT ASSIGNEE(S): Chevron Phillips Chemical Company LP (U.S.  
corporation)

	NUMBER	KIND	DATE
PATENT INFORMATION:	US 20060036110	A1	20060216
APPLICATION INFO.:	US 2005-60696	A1	20050217 (11)

	NUMBER	DATE
PRIORITY INFORMATION:	US 2004-545260P	20040217 (60)
	US 2004-561614P	20040413 (60)
	US 2004-561685P	20040413 (60)
	US 2004-561855P	20040413 (60)
DOCUMENT TYPE:	Utility	
FILE SEGMENT:	APPLICATION	
LEGAL REPRESENTATIVE:	Kimberly L. Brown, Chevron Phillips Chemical Company LP, 10001 Six Pines Drive, The Woodlands, TX, 77380, US	
NUMBER OF CLAIMS:	24	
EXEMPLARY CLAIM:	1	
NUMBER OF DRAWINGS:	14 Drawing Page(s)	
LINE COUNT:	6358	
CAS INDEXING IS AVAILABLE FOR THIS PATENT.		

L11 ANSWER 31 OF 85 USPATFULL on STN  
SUMM The invention includes a process for the manufacturing of a  
compound of  
Formula I or its ester or salt thereof, ##STR2## wherein  
Z.sup.1,  
Z.sup.2, Z.sup.3, and Z.sup.4 are independently selected from the  
group  
consisting of hydrogen and alkyl, said alkyl optionally  
substituted by  
hydroxy, alkyl, alkenyl, acyl, nitro, amino, halo, carboxy and  
cyano;  
Z.sup.5 and Z.sup.6 are the same or different and independently  
selected from  
the group consisting of alkyl, alkenyl, and aryl all of which can  
be  
optionally substituted by hydroxy, alkyl, alkenyl, acyl, nitro,  
amino,

halo, carboxy and cyano;  
Z<sup>sup.5</sup> and Z<sup>sup.6</sup> can come together to form a carbocyclic ring;  
M is selected from the group consisting of hydrogen, an optionally substituted  
unsaturated alkyl having from 1 to 10 carbon atoms, and an  
optionally substituted saturated alkyl having from 1 to 10 carbon atoms,  
said optionally substituted unsaturated alkyl and optionally substituted  
saturated alkyl optionally containing a polar or charged  
functionality;  
or M is selected from the group consisting of hydrogen, an optionally substituted unsaturated acyl having from 1 to 18 carbon atoms,  
and an optionally substituted saturated acyl having from 1 to 18 carbon atoms,  
said optionally substituted unsaturated acyl and optionally substituted  
saturated acyl optionally containing a polar or charged  
functionality;  
J is selected from the group consisting of an optionally substituted unsaturated alkyl having from 1 to 10 carbon atoms, and an  
optionally substituted saturated alkyl having from 1 to 10 carbon atoms,  
said optionally substituted unsaturated alkyl and optionally substituted  
saturated alkyl optionally containing a polar or charged  
functionality;  
or J is selected from the group consisting of an optionally substituted unsaturated acyl having from 1 to 18 carbon atoms and an  
optionally substituted saturated acyl having from 1 to 18 carbon atoms, said  
optionally substituted unsaturated acyl and optionally substituted  
saturated acyl optionally containing a polar or charged  
functionality;  
the process comprising:  
reacting a compound of Formula II, ##STR3## wherein Z<sup>sup.1</sup>, Z<sup>sup.2</sup>, Z<sup>sup.3</sup>, Z<sup>sup.4</sup>, Z<sup>sup.5</sup> and Z<sup>sup.6</sup> are as previously defined,  
with a compound of Formula III, ##STR4## wherein Y is R<sup>sup.2</sup> or NR<sup>sup.2</sup>R<sup>sup.5</sup>;  
R<sup>sup.1</sup>, R<sup>sup.2</sup>, R<sup>sup.3</sup> and R<sup>sup.4</sup> and R<sup>sup.5</sup> are independently selected  
from an optionally substituted C<sub>sub.1-10</sub> alkyl or an optionally substituted C<sub>sub.2-10</sub> alkenyl;  
R<sup>sup.1</sup> and R<sup>sup.2</sup> can optionally come together to form a ring;  
R<sup>sup.3</sup> and R<sup>sup.4</sup> can optionally come together to form a ring; and  
a compound selected from the group consisting of a saturated or unsaturated acyl halide, saturated or unsaturated carboxylic acid anhydride and a saturated or unsaturated activated carboxylic acid ester, all of which may optionally be substituted by one or more substituents selected from the group consisting of protected hydroxy,

alkyl, alkenyl, acyl, nitro, protected amino, amino, halo, protected carboxy and cyano; or, a compound selected the group consisting of a saturated or unsaturated alkyl halide, saturated or unsaturated alkyl-O-sulfonyl alkyl, a saturated or unsaturated alkyl-O-sulfonyl aryl, a saturated or unsaturated alkyl-O-acyl, and a saturated or unsaturated \*\*\*epoxide\*\*\*, all of which may optionally be substituted by one or more substituents selected from the group consisting of protected hydroxy, alkyl, alkenyl, acyl, nitro, protected amino, halo, protected carboxy, \*\*\*epoxide\*\*\* and cyano; and, separating and isolating the compound of Formula I.

SUMM The terms "alkyl" or "alk", alone or in combination, unless otherwise specified, means a saturated straight or branched primary, secondary, or tertiary hydrocarbon from 1 to 16 carbon atoms, including, but not limited to methyl, ethyl, propyl, isopropyl, butyl, isobutyl, t-butyl, and sec-butyl. The alkyl group may be optionally substituted where possible with any moiety that does not otherwise interfere with the reaction or that provides an improvement in the process, including but not limited to halo, haloalkyl, hydroxyl, carboxyl, acyl, aryl, acyloxy, amino, amido, carboxyl derivatives, alkylamino, dialkylamino, arylamino, alkoxy, aryloxy, nitro, cyano, sulfonic acid, \*\*\*thiol\*\*\*, imine, sulfonyl, sulfanyl, sulfinyl, sulfamonyl, ester, carboxylic acid, amide, phosphonyl, phosphinyl, phosphoryl, phosphine, thioester, thioether, acid halide, anhydride, oxime, hydrozine, carbamate, phosphonic acid, phosphonate, either unprotected, or protected as necessary, as known to those skilled in the art.

SUMM The term "alkenyl", alone or in combination, means a non-cyclic alkyl of 2 to 10 carbon atoms having one or more unsaturated carbon-carbon bonds. The alkenyl group may be optionally substituted where possible with any moiety that does not otherwise interfere with the reaction or that provides an improvement in the process, including but not limited to halo, haloalkyl, hydroxyl, carboxyl, acyl, aryl, acyloxy, amino, amido, carboxyl derivatives, alkylamino, dialkylamino, arylamino, alkoxy, aryloxy, nitro, cyano, sulfonic acid, \*\*\*thiol\*\*\*, imine,

sulfonyl, sulfanyl, sulfinyl, sulfamonyl, ester, carboxylic acid, amide, phosphonyl, phosphinyl, phosphoryl, phosphine, thioester, thioether, acid halide, anhydride, oxime, hydrozine, carbamate, phosphonic acid, phosphonate, either unprotected, or protected as necessary, as known to those skilled in the art.

SUMM The term "alkynyl", alone or in combination, means a non-cyclic alkyl of 2 to 10 carbon atoms having one or more triple carbon-carbon bonds, including but not limited to ethynyl and propynyl. The alkynyl group may be optionally substituted where possible with any moiety that does not otherwise interfere with the reaction or that provides an improvement in the process, including but not limited to halo, haloalkyl, hydroxyl, carboxyl, acyl, aryl, acyloxy, amino, amido, carboxyl derivatives, alkylamino, dialkylamino, arylamino, alkoxy, aryloxy, nitro, cyano, sulfonic acid, \*\*\*thiol\*\*\*, imine, sulfonyl, sulfanyl, sulfinyl, sulfamonyl, ester, carboxylic acid, amide, phosphonyl, phosphinyl, phosphoryl, phosphine, thioester, thioether, acid halide, anhydride, oxime, hydrozine, carbamate, phosphonic acid, phosphonate, either unprotected, or protected as necessary, as known to those skilled in the art.

SUMM The term "aryl", alone or in combination, means a carbocyclic aromatic system containing one, two or three rings wherein such rings may be attached together in a pendent manner or may be fused. The "aryl" group can be optionally substituted where possible with one or more of the moieties selected from the group consisting of alkyl, alkenyl, alkynyl, heteroaryl, heterocyclic, carbocycle, alkoxy, oxo, aryloxy, arylalkoxy, cycloalkyl, tetrazolyl, heteroaryloxy; heteroarylalkoxy, carbohydrate, amino acid, amino acid esters, amino acid amides, alditol, halogen, haloalkylthi, haloalkoxy, haloalkyl, hydroxyl, carboxyl, acyl, acyloxy, amino, aminoalkyl, aminoacyl, amido, alkylamino, dialkylamino, arylamino, nitro, cyano, \*\*\*thiol\*\*\*, imide, sulfonic acid, sulfate, sulfonate, sulfonyl, alkylsulfonyl, aminosulfonyl, alkylsulfonylamino,



haloalkylsulfonyl, sulfanyl, sulfinyl, sulfamoyl, carboxylic ester, carboxylic acid, amide, phosphonyl, phosphinyl, phosphoryl, thioester, thioether, oxime, hydrazine, carbamate, phosphonic acid, phosphate, phosphonate, phosphinate, sulfonamido, carboxamido, hydroxamic acid, sulfonylimide or any other desired functional group that does not inhibit the pharmacological activity of this compound, either unprotected, or protected as necessary, as known to those skilled in the art. In addition, adjacent groups on an "aryl" ring may combine to form a 5- to 7-membered saturated or partially unsaturated carbocyclic, aryl, heteroaryl or heterocyclic ring, which in turn may be substituted as above.

SUMM The term "substituted", means that one or more hydrogen on the designated atom or substituent is replaced with a selection from the indicated group, provided that the designated atom's normal valency is not exceeded, and that the substitution results in a stable compound. When a substituent is "oxo" (keto) (i.e., .dbd.O), then 2 hydrogens on the atom are replaced. If the term is used without an indicating group, an appropriate substituent known by those skilled in the art may be substituted, including, but not limited to, hydroxyl, alkyl, alkenyl, acyl, nitro, protected amino, halo, protected carboxy, \*\*\*epoxide\*\*\*, and cyano.

SUMM The term "polar or charged functionality" means a polar or charged group attached in place of one or more hydrogen atoms. Non limiting examples include carboxy, hydroxy, amino, \*\*\*epoxide\*\*\*, etc.

SUMM The term " \*\*\*epoxide\*\*\* " means the radical ##STR7## wherein all R groups are independently selected from hydrogen, alkyl, aryl and arylalkyl wherein said alkyl, aryl and arylalkyl may optionally be substituted with a polar functionality.

DETD In a broad description, the invention encompasses the method of manufacturing a compound of Formula I or its ester or salt thereof, ##STR13## wherein Z.sup.1, Z.sup.2, Z.sup.3, and Z.sup.4 are independently selected from the group consisting of hydrogen and alkyl, said alkyl optionally substituted by hydroxy, alkyl, alkenyl, acyl,

nitro, amino, halo, carboxy and cyano;  
Z.sup.5 and Z.sup.6 are the same or different and independently  
selected from  
the group consisting of alkyl, alkenyl, and aryl all of which can  
be  
optionally substituted by hydroxy, alkyl, alkenyl, acyl, nitro,  
amino,  
halo, carboxy and cyano;  
Z.sup.5 and Z.sup.6 can come together to form a carbocyclic ring;  
M is selected from the group consisting of hydrogen, an optionally  
substituted  
unsaturated alkyl having from 1 to 10 carbon atoms, and an  
optionally  
substituted saturated alkyl having from 1 to 10 carbon atoms,  
said  
optionally substituted unsaturated alkyl and optionally  
substituted  
saturated alkyl optionally containing a polar or charged  
functionality;  
or M is selected from the group consisting of hydrogen, an optionally  
substituted unsaturated acyl having from 1 to 18 carbon atoms,  
and an  
optionally substituted saturated acyl having from 1 to 18 carbon  
atoms,  
said optionally substituted unsaturated acyl and optionally  
substituted  
saturated acyl optionally containing a polar or charged  
functionality;  
J is selected from the group consisting of an optionally substituted  
unsaturated alkyl having from 1 to 10 carbon atoms, and an  
optionally  
substituted saturated alkyl having from 1 to 10 carbon atoms,  
said  
optionally substituted unsaturated alkyl and optionally  
substituted  
saturated alkyl optionally containing a polar or charged  
functionality;  
or J is selected from the group consisting of an optionally substituted  
unsaturated acyl having from 1 to 18 carbon atoms and an  
optionally  
substituted saturated acyl having from 1 to 18 carbon atoms, said  
optionally substituted unsaturated acyl and optionally  
substituted  
saturated acyl optionally containing a polar or charged  
functionality;  
the process comprising:  
reacting a compound of Formula II, ##STR14## wherein Z.sup.1,  
Z.sup.2,  
Z.sup.3, Z.sup.4, Z.sup.5 and Z.sup.6 are as previously defined,  
with a  
compound of Formula III, ##STR15## wherein Y is R.sup.2 or  
NR.sup.2R.sup.5;  
R.sup.1, R.sup.2, R.sup.3 and R.sup.4 and R.sup.5 are independently  
selected  
from an optionally substituted C.sub.1-C.sub.10 alkyl or an  
optionally  
substituted C.sub.2-C.sub.10 alkenyl;  
R.sup.1 and R.sup.2 can optionally come together to form a ring;  
R.sup.3 and R.sup.4 can optionally come together to form a ring; and  
a

compound selected from the group consisting of a saturated or unsaturated acyl halide, saturated or unsaturated carboxylic acid anhydride and a saturated or unsaturated activated carboxylic acid ester, all of which may optionally be substituted by one or more selected from the group consisting of protected hydroxy, alkyl, alkenyl, acyl, nitro, protected amino, amino, halo, protected carboxy and cyano; or a compound selected the group consisting of a saturated or unsaturated alkyl halide, saturated or unsaturated alkyl-O-sulfonyl alkyl, a saturated or unsaturated alkyl-O-acyl, and a saturated or unsaturated \*\*\*epoxide\*\*\*, all of which may optionally be substituted by one or more selected from the group consisting of protected hydroxy, alkyl, alkenyl, acyl, nitro, protected amino, halo, protected carboxy, \*\*\*epoxide\*\*\* and cyano; and separating and isolating said compound of Formula I.

DETD In a 2.sup.nd embodiment, the invention is represented by the process to manufacture a compound of Formula I or its ester or salt thereof, ##STR16## wherein Z.sup.1, Z.sup.2, Z.sup.3, and Z.sup.4 are independently selected from the group consisting of hydrogen and alkyl, said alkyl optionally substituted by hydroxy, alkyl, alkenyl, acyl, nitro, amino, halo, carboxy and cyano; Z.sup.5 and Z.sup.6 are the same or different and independently selected from the group consisting of alkyl, alkenyl, and aryl all of which can be optionally substituted by hydroxy, alkyl, alkenyl, acyl, nitro, amino, halo, carboxy and cyano; Z.sup.5 and Z.sup.6 can come together to form a carbocyclic ring; M is selected from the group consisting of hydrogen, an optionally substituted unsaturated alkyl having from 1 to 10 carbon atoms, and an optionally substituted saturated alkyl having from 1 to 10 carbon atoms, said optionally substituted unsaturated alkyl and optionally substituted saturated alkyl optionally containing a polar or charged functionality; and J is selected from the group consisting of an optionally substituted unsaturated alkyl having from 1 to 10 carbon atoms, and an optionally substituted saturated alkyl having from 1 to 10 carbon atoms, said optionally substituted unsaturated alkyl and optionally substituted

saturated alkyl optionally containing a polar or charged functionality;  
the process comprising:  
reacting a compound of Formula II, ##STR17## wherein Z.sup.1, Z.sup.2, Z.sup.3, Z.sup.4, Z.sup.5 and Z.sup.6 are as previously defined, with a compound of Formula III, ##STR18## wherein Y is R.sup.2 or NR.sup.2R.sup.5;  
R.sup.1, R.sup.2, R.sup.3 and R.sup.4 and R.sup.5 are independently selected  
from an optionally substituted C.sub.1-C.sub.10 alkyl or an optionally substituted C.sub.2-C.sub.10 alkenyl;  
R.sup.1 and R.sup.2 can optionally come together to form a ring;  
R.sup.3 and R.sup.4 can optionally come together to form a ring; and  
a compound selected the group consisting of a saturated or unsaturated alkyl halide, saturated or unsaturated alkyl-O-sulfonyl alkyl, a saturated or unsaturated alkyl-O-sulfonyl aryl, a saturated or unsaturated alkyl-O-acyl, and a saturated or unsaturated \*\*\*epoxide\*\*\*, all of which may optionally be substituted by one or more selected from the group consisting of protected hydroxy, alkyl, alkenyl, acyl, nitro, protected amino, halo, protected carboxy, \*\*\*epoxide\*\*\* and cyano; and separating and isolating said compound of Formula I.

DETD In a 3.sup.rd embodiment, the invention is represented by the process to manufacture a compound of Formula IV or its ester or salt thereof, ##STR19## wherein J is selected from the group consisting of an optionally substituted unsaturated alkyl having from 1 to 10 carbon atoms, and an optionally substituted saturated alkyl having from 1 to 10 carbon atoms, said optionally substituted unsaturated alkyl and optionally substituted saturated alkyl optionally containing a polar or charged functionality;  
the process comprising:  
reacting a compound of Formula V, ##STR20## with a compound of Formula III, ##STR21## wherein Y is R.sup.2 or NR.sup.2R.sup.5;  
R.sup.1, R.sup.2, R.sup.3 and R.sup.4 and R.sup.5 are independently selected  
from an optionally substituted C.sub.1-C.sub.10 alkyl or an optionally substituted C.sub.2-C.sub.10 alkenyl;  
R.sup.1 and R.sup.2 can optionally come together to form a ring;  
R.sup.3 and R.sup.4 can optionally come together to form a ring; and  
a compound selected from the group consisting of a saturated or unsaturated alkyl halide, saturated or unsaturated alkyl-O-sulfonyl alkyl, a saturated or unsaturated alkyl-O-sulfonyl aryl, a

saturated or  
 unsaturated alkyl-O-acyl, and a saturated or unsaturated  
 \*\*\*epoxide\*\*\*  
 , all of which may optionally be substituted by one or more  
 substituents  
 selected from the group consisting of protected hydroxy, alkyl,  
 alkenyl,  
 acyl, nitro, protected amino, halo, protected carboxy,  
 \*\*\*epoxide\*\*\*  
 and cyano; and separating and isolating said compound of Formula  
 IV.  
 CLM What is claimed is:  
 10. A process for manufacturing a compound of Formula I or its  
 ester or  
 salt thereof, ##STR77## wherein Z.<sup>sup.1</sup>, Z.<sup>sup.2</sup>, Z.<sup>sup.3</sup>,  
 and  
 Z.<sup>sup.4</sup> are independently selected from the group consisting of  
 hydrogen  
 and alkyl, said alkyl optionally substituted by hydroxy, alkyl,  
 alkenyl,  
 acyl, nitro, amino, halo, carboxy and cyano; Z.<sup>sup.5</sup> and Z.<sup>sup.6</sup>  
 are  
 the same or different and independently selected from the group  
 consisting of alkyl, alkenyl, and aryl all of which can be  
 optionally  
 substituted by hydroxy, alkyl, alkenyl, acyl, nitro, amino, halo,  
 carboxy and cyano; Z.<sup>sup.5</sup> and Z.<sup>sup.6</sup> can come together to form  
 a  
 carbocyclic ring; M is selected from the group consisting of  
 hydrogen,  
 an optionally substituted unsaturated alkyl having from 1 to 10  
 carbon  
 atoms, and an optionally substituted saturated alkyl having from  
 1 to 10  
 carbon atoms, said optionally substituted unsaturated alkyl and  
 optionally substituted saturated alkyl optionally containing a  
 polar or  
 charged functionality; and J is selected from the group  
 consisting of  
 an optionally substituted unsaturated alkyl having from 1 to 10  
 carbon  
 atoms, and an optionally substituted saturated alkyl having from  
 1 to 10  
 carbon atoms, said optionally substituted unsaturated alkyl and  
 optionally substituted saturated alkyl optionally containing a  
 polar or  
 charged functionality; the process comprising: reacting a  
 compound of  
 Formula II ##STR78## wherein Z.<sup>sup.1</sup>, Z.<sup>sup.2</sup>, Z.<sup>sup.3</sup>,  
 Z.<sup>sup.4</sup>,  
 Z.<sup>sup.5</sup> and Z.<sup>sup.6</sup> are as previously defined, with a compound  
 of  
 Formula III, ##STR79## wherein Y is R.<sup>sup.2</sup> or  
 NR.<sup>sup.2</sup>R.<sup>sup.5</sup>;  
 R.<sup>sup.1</sup>, R.<sup>sup.2</sup>, R.<sup>sup.3</sup> and R.<sup>sup.4</sup> and R.<sup>sup.5</sup> are  
 independently  
 selected from an optionally substituted C.sub.1-C.sub.10 alkyl or  
 an  
 optionally substituted C.sub.2-C.sub.10 alkenyl; R.<sup>sup.1</sup> and  
 R.<sup>sup.2</sup>

can optionally come together to form a ring; R.sup.3 and R.sup.4  
can optionally come together to form a ring; and a compound selected  
the group consisting of a saturated or unsaturated alkyl halide,  
saturated or unsaturated alkyl-O-sulfonyl alkyl, a saturated or unsaturated  
alkyl-O-sulfonyl aryl, a saturated or unsaturated alkyl-O-acyl,  
and a saturated or unsaturated \*\*\*epoxide\*\*\*, all of which may  
optionally be substituted by one or more substituents selected from the  
group consisting of protected hydroxy, alkyl, alkenyl, acyl, nitro,  
protected amino, halo, protected carboxy, \*\*\*epoxide\*\*\* and cyano; and  
separating and isolating the compound of Formula I.

CLM What is claimed is:

11. The process of claim 10 to manufacture a compound of Formula  
IV or

its ester or salt thereof, ##STR80## wherein J is selected  
from the group consisting of an optionally substituted unsaturated alkyl  
having

from 1 to 10 carbon atoms, and an optionally substituted  
saturated alkyl having from 1 to 10 carbon atoms, said optionally substituted  
unsaturated alkyl and optionally substituted saturated alkyl

optionally containing a polar or charged functionality; the process  
comprising:

reacting a compound of Formula V ##STR81## with a compound  
of

Formula III, ##STR82## wherein Y is R.sup.2 or  
NR.sup.2R.sup.5;

R.sup.1, R.sup.2, R.sup.3 and R.sup.4 and R.sup.5 are  
independently

selected from an optionally substituted C.sub.1-C.sub.10 alkyl or  
an

optionally substituted C.sub.2-C.sub.10 alkenyl; R.sup.1 and  
R.sup.2

can optionally come together to form a ring; R.sup.3 and R.sup.4  
can

optionally come together to form a ring; and a compound selected  
from

the group consisting of a saturated or unsaturated alkyl halide,  
saturated or unsaturated alkyl-O-sulfonyl alkyl, a saturated or  
unsaturated alkyl-O-sulfonyl aryl, a saturated or unsaturated  
alkyl-O-acyl, and a saturated or unsaturated \*\*\*epoxide\*\*\*,

all of which may optionally be substituted by one or more substituents  
selected from the group consisting of protected hydroxy, alkyl, alkenyl,  
acyl,

nitro, protected amino, halo, protected carboxy, \*\*\*epoxide\*\*\*  
and

cyano; and separating and isolating the compound of Formula IV.

IT \*\*\*3001-72-7\*\*\*, Dbn \*\*\*6674-22-2\*\*\*, Dbu

(prepn. of esters of probucol and derivs. thereof using acid anhydrides

in the presence of DBU or DBN)

ACCESSION NUMBER: 2005:306544 USPATFULL <<LOGINID::20090306>>

TITLE: Process of preparing esters and ethers of

probucol and

derivatives thereof

INVENTOR(S): Weingarten, M. David, Cumming, GA, UNITED STATES

	NUMBER	KIND	DATE
PATENT INFORMATION:	US 20050267187	A1	20051201
	US 7294737	B2	20071113
APPLICATION INFO.:	US 2005-111194	A1	20050420 (11)

	NUMBER	DATE
PRIORITY INFORMATION:	US 2004-564267P	20040420 (60)
DOCUMENT TYPE:	Utility	
FILE SEGMENT:	APPLICATION	
LEGAL REPRESENTATIVE:	KING & SPALDING LLP, 191 PEACHTREE STREET, N.E., 45TH FLOOR, ATLANTA, GA, 30303-1763, US	
NUMBER OF CLAIMS:	11	
EXEMPLARY CLAIM:	1	
LINE COUNT:	1405	

CAS INDEXING IS AVAILABLE FOR THIS PATENT.

L11 ANSWER 36 OF 85 USPATFULL on STN

TI \*\*\*Thiol\*\*\* ester compositions and processes for making and using

same

AB \*\*\*Thiol\*\*\* ester compositions, methods of making the

\*\*\*thiol\*\*\*

ester compositions, and methods of using the \*\*\*thiol\*\*\*

ester

compositions are provided. In some embodiments, the \*\*\*thiol\*\*\* ester compositions include \*\*\*thiol\*\*\* esters, hydroxy

\*\*\*thiol\*\*\*

esters and cross-linked \*\*\*thiol\*\*\* esters. The \*\*\*thiol\*\*\* ester composition can be used to produce cross-linked

\*\*\*thiol\*\*\*

esters, sulfonic acid-containing esters, sulfonate containing

esters and

thioacrylate containing esters. The \*\*\*thiol\*\*\* ester

compositions

can be used to produce polythiourethanes. The polythiourethanes

can be

used in fertilizers and fertilizer coatings.

SUMM The invention relates to \*\*\*thiol\*\*\* containing ester

compositions

generally made from a reaction of unsaturated ester compositions

and a

material capable of forming a \*\*\*thiol\*\*\* group. The

invention also

relates to the processes for preparing such \*\*\*thiol\*\*\*

containing

compositions and uses for the \*\*\*thiol\*\*\* containing

compositions.

SUMM The present invention advantageously provides \*\*\*thiol\*\*\*  
containing compositions and methods of making such compositions.

In addition to the compositions and methods of making such  
compositions,  
products that include such compositions are also provided.

SUMM As an embodiment of the present invention, a \*\*\*thiol\*\*\*  
ester  
composition is advantageously provided. In this embodiment, the  
\*\*\*thiol\*\*\* ester composition includes \*\*\*thiol\*\*\* ester  
molecules  
that have an average of at least 1.5 ester groups per  
\*\*\*thiol\*\*\*  
ester molecule. The \*\*\*thiol\*\*\* ester molecules also have an  
average  
of at least 1.5 \*\*\*thiol\*\*\* groups per \*\*\*thiol\*\*\* ester  
molecule. The \*\*\*thiol\*\*\* ester molecules also have a molar  
ratio of  
cyclic sulfides to \*\*\*thiol\*\*\* groups of less than 1.5.

SUMM In some aspects, the \*\*\*thiol\*\*\* ester molecules have a  
molar ratio  
of cyclic sulfides to \*\*\*thiol\*\*\* groups ranging from 0 to  
1.0. In  
some aspects, the \*\*\*thiol\*\*\* ester molecules have an average  
ranging from 1.5 to 9 \*\*\*thiol\*\*\* groups per \*\*\*thiol\*\*\*  
ester  
molecule. In some embodiments, the \*\*\*thiol\*\*\* ester  
molecules have  
a molar ratio of carbon-carbon double bonds to \*\*\*thiol\*\*\*  
groups of  
less than 1.5.

SUMM The amount of \*\*\*thiol\*\*\* sulfur or \*\*\*mercaptan\*\*\*  
sulfur  
contained within the \*\*\*thiol\*\*\* ester molecules can also  
vary. For  
example, in some embodiments, the \*\*\*thiol\*\*\* ester molecules  
have  
an average of greater than 5 weight percent \*\*\*thiol\*\*\*  
sulfur. In  
other embodiments, the \*\*\*thiol\*\*\* ester molecules have an  
average  
ranging from 8 to 10 weight percent \*\*\*thiol\*\*\* sulfur. In  
some  
embodiments, the \*\*\*thiol\*\*\* ester molecules have an average  
of less  
than 30 mole percent sulfur, which is present as cyclic sulfides.  
Alternatively, the \*\*\*thiol\*\*\* ester molecules have an  
average of  
less than 2 mole percent sulfur present as cyclic sulfides.

SUMM In some embodiments, the \*\*\*thiol\*\*\* ester molecules are  
produced  
from unsaturated esters that have an average of less than 25  
weight  
percent of side chains that include 3 contiguous methylene  
interrupted  
carbon-carbon double bonds. In another aspect, greater than 40



percent of the total side chains contained within the \*\*\*thiol\*\*\* ester molecules contain sulfur.

SUMM In addition to the \*\*\*thiol\*\*\* ester composition, a process for producing the \*\*\*thiol\*\*\* ester composition is advantageously provided as another embodiment of the present invention. To produce the \*\*\*thiol\*\*\* ester composition, hydrogen sulfide is contacted with an unsaturated ester composition. The unsaturated ester composition includes unsaturated esters that have an average of at least 1.5 ester groups per unsaturated ester molecule. The unsaturated esters also have an average of at least 1.5 carbon-carbon double bonds per unsaturated ester molecule. The hydrogen sulfide and the unsaturated esters are reacted to produce or form the \*\*\*thiol\*\*\* ester composition. The \*\*\*thiol\*\*\* ester composition advantageously includes \*\*\*thiol\*\*\* ester molecules that have a molar ratio of cyclic sulfides to \*\*\*thiol\*\*\* groups of less than 1.5.

SUMM Another process for producing the \*\*\*thiol\*\*\* ester composition is advantageously provided as another embodiment of the present invention. In this process embodiment, the hydrogen sulfide and the unsaturated ester composition are contacted. The unsaturated ester composition includes unsaturated esters having an average of at least 1.5 ester groups per unsaturated ester molecule and having an average of at least 1.5 carbon-carbon double bonds per unsaturated ester molecule. The hydrogen sulfide and the unsaturated esters are then reacted in a substantial absence of a solvent to form the \*\*\*thiol\*\*\* ester composition. The \*\*\*thiol\*\*\* ester composition includes \*\*\*thiol\*\*\* ester molecules. The \*\*\*thiol\*\*\* ester composition advantageously includes \*\*\*thiol\*\*\* ester molecules that have a molar ratio of cyclic sulfides to \*\*\*thiol\*\*\* groups of less than 1.5.

SUMM The resulting \*\*\*thiol\*\*\* ester molecules produced by this process possess advantageous characteristics. For example, in some embodiments, the \*\*\*thiol\*\*\* ester molecules have a molar ratio of the hydrogen

sulfide to carbon-carbon double bonds of greater than 2. As another

example, in other embodiments, the \*\*\*thiol\*\*\* ester molecules have

an average of greater than 5 weight percent \*\*\*thiol\*\*\* sulfur. In

some aspects, greater than 40 percent of the \*\*\*thiol\*\*\* ester

molecule total side chains contain sulfur.

SUMM As another embodiment of the present invention, another process for

preparing the \*\*\*thiol\*\*\* ester composition is advantageously provided. In this embodiment, a polyol composition and a \*\*\*thiol\*\*\*

carboxylic acid composition are contacted and reacted to produce the

\*\*\*thiol\*\*\* ester composition. The \*\*\*thiol\*\*\* ester composition

includes \*\*\*thiol\*\*\* ester molecules having an average of at least

1.5 ester groups per \*\*\*thiol\*\*\* ester molecule and having an average of at least 1.5 \*\*\*thiol\*\*\* groups per \*\*\*thiol\*\*\* ester

molecule.

SUMM In addition to the \*\*\*thiol\*\*\* ester composition, other compositions are advantageously provided as embodiments of the present

invention. For example, a hydroxy \*\*\*thiol\*\*\* ester composition is

provided as another embodiment of the present invention. The hydroxyl

\*\*\*thiol\*\*\* ester composition includes hydroxy \*\*\*thiol\*\*\* ester

molecules having an average of at least 1.5 ester groups per hydroxy

\*\*\*thiol\*\*\* ester molecule and having an average of at least 1.5

.alpha.-hydroxy \*\*\*thiol\*\*\* groups per hydroxy \*\*\*thiol\*\*\* ester

molecule.

SUMM As described herein, the .alpha.-hydroxy \*\*\*thiol\*\*\* groups contain

an alcohol or hydroxy group and a \*\*\*thiol\*\*\* group within the same

group. In embodiments of the present invention, the .alpha.-hydroxy

\*\*\*thiol\*\*\* groups can be replaced with separate alcohol and \*\*\*thiol\*\*\*

.alpha.-hydroxy groups. In these embodiments, the same number of .alpha.-hydroxy

\*\*\*thiol\*\*\* groups. For example, in some embodiments, the

hydroxy \*\*\*thiol\*\*\* ester molecules have an average of at least 1.5 .alpha.-hydroxy

\*\*\*thiol\*\*\* groups. In embodiments that contain

separate alcohol and \*\*\*thiol\*\*\* groups, the hydroxy \*\*\*thiol\*\*\*

ester molecules would contain an average of at least 1.5 alcohol

groups

and an average of at least 1.5 \*\*\*thiol\*\*\* groups.

SUMM In some aspects, the hydroxy \*\*\*thiol\*\*\* ester molecules have an

average ranging from 1.5 to 9 .alpha.-hydroxy \*\*\*thiol\*\*\* groups per hydroxy \*\*\*thiol\*\*\* ester molecule. In some embodiments, the \*\*\*thiol\*\*\* ester molecules have a molar ratio of carbon-carbon double bonds to \*\*\*thiol\*\*\* groups of less than 1.5.

SUMM In some embodiments, the \*\*\*thiol\*\*\* ester molecules are produced

from unsaturated esters that have an average of less than 25 weight percent of side chains that include 3 contiguous methylene interrupted carbon-carbon double bonds. In another aspect, greater than 40 percent of the total side chains contained within the .alpha.-hydroxy \*\*\*thiol\*\*\* ester molecules contain sulfur.

SUMM The amount of \*\*\*thiol\*\*\* sulfur contained within the hydroxy

\*\*\*thiol\*\*\* ester molecules can also vary. For example, in some embodiments, the hydroxy \*\*\*thiol\*\*\* ester molecules have an average of greater than 5 weight percent \*\*\*thiol\*\*\* sulfur. In other embodiments, the hydroxy \*\*\*thiol\*\*\* ester molecules have an average ranging from 8 to 10 weight percent \*\*\*thiol\*\*\* sulfur.

SUMM In some embodiments, the hydroxy \*\*\*thiol\*\*\* ester molecules have a

molar ratio of \*\*\*epoxide\*\*\* groups to the .alpha.-hydroxy \*\*\*thiol\*\*\* groups of less than 2. In other aspects, the composition is substantially free of \*\*\*epoxide\*\*\* groups.

SUMM In addition to the hydroxy \*\*\*thiol\*\*\* ester composition, methods

or processes for making the hydroxy \*\*\*thiol\*\*\* ester composition are advantageously provided as embodiments of the present invention. In an embodiment, a process for preparing the hydroxy \*\*\*thiol\*\*\* ester

composition is provided that includes the step of contacting the hydrogen sulfide and an epoxidized unsaturated ester composition.

The epoxidized unsaturated ester composition includes epoxidized unsaturated esters having an average of at least 1.5 ester groups per epoxidized unsaturated ester molecule and having an average of at least 1.5 \*\*\*epoxide\*\*\* groups per epoxidized unsaturated ester molecule. The

hydrogen sulfide and the epoxidized unsaturated esters are then

reacted  
to form the hydroxy \*\*\*thiol\*\*\* ester composition.

SUMM In some embodiments, a molar ratio of the hydrogen sulfide to  
\*\*\*epoxide\*\*\* groups in the epoxidized unsaturated esters is  
greater than 1.

SUMM Another process for preparing the hydroxy \*\*\*thiol\*\*\* ester  
composition is advantageously provided as another embodiment of  
the present invention. In this process embodiment, a polyol  
composition and a hydroxy \*\*\*thiol\*\*\* carboxylic acid composition are  
contacted and reacted to produce the hydroxy \*\*\*thiol\*\*\* ester composition.  
In this embodiment, the hydroxy \*\*\*thiol\*\*\* ester composition  
includes hydroxy \*\*\*thiol\*\*\* ester molecules having an average of at  
least 1.5 ester groups per hydroxy \*\*\*thiol\*\*\* ester molecule and  
having an average of at least 1.5 .alpha.-hydroxy \*\*\*thiol\*\*\* groups  
per hydroxy \*\*\*thiol\*\*\* ester molecule.

SUMM A cross-linked \*\*\*thiol\*\*\* ester composition is  
advantageously provided as another embodiment of the present invention. The  
cross-linked \*\*\*thiol\*\*\* ester composition includes  
\*\*\*thiol\*\*\* ester oligomers having at least two \*\*\*thiol\*\*\* ester  
monomers connected by a polysulfide linkage having a structure --  
S.sub.Q--,  
wherein Q is greater than 1. In some embodiments, the  
\*\*\*thiol\*\*\* ester oligomers have at least three \*\*\*thiol\*\*\* ester  
monomers connected by polysulfide linkages. In another aspect, the  
\*\*\*thiol\*\*\* ester oligomers have from 3 to 20 \*\*\*thiol\*\*\* ester monomers  
connected by polysulfide linkages.

SUMM In an aspect, the cross-linked \*\*\*thiol\*\*\* ester composition  
includes both \*\*\*thiol\*\*\* ester monomers and \*\*\*thiol\*\*\*  
ester oligomers. In some embodiments, the \*\*\*thiol\*\*\* ester  
monomers and \*\*\*thiol\*\*\* ester oligomers have a total \*\*\*thiol\*\*\*  
sulfur content ranging from 0.5 to 8 weight percent; or alternatively,  
ranging from 8 to 15 weight percent. The combined \*\*\*thiol\*\*\* ester  
monomers and \*\*\*thiol\*\*\* ester oligomers can have an average molecular  
weight greater than 2000; or alternatively, in a range from 2000 to  
20,000.

SUMM As another embodiment of the present invention, a cross-linked  
\*\*\*thiol\*\*\* ester composition produced by the process  
comprising the  
steps of contacting the \*\*\*thiol\*\*\* ester composition with an  
oxidizing agent and reacting the \*\*\*thiol\*\*\* ester and the  
agent to form \*\*\*thiol\*\*\* ester oligomers is advantageously  
provided. In this embodiment, the \*\*\*thiol\*\*\* ester oligomers  
have  
at least two \*\*\*thiol\*\*\* ester monomers connected by a  
polysulfide  
linkage having a structure --S.sub.Q--, wherein Q is greater than  
1.

SUMM A process to produce the cross-linked \*\*\*thiol\*\*\* ester  
composition  
is also advantageously provided as another embodiment of the  
present  
invention. In this process, a \*\*\*thiol\*\*\* ester composition  
is  
contacted and reacted with an oxidizing agent to form  
\*\*\*thiol\*\*\*  
ester oligomers having at least two \*\*\*thiol\*\*\* ester  
monomers  
connected by a polysulfide linkage having a structure --  
S.sub.Q--,  
wherein Q is greater than 1. In some embodiments, the oxidizing  
agent is  
elemental sulfur, oxygen, or hydrogen peroxide. In an aspect, the  
oxidizing agent is elemental sulfur.

SUMM In an aspect, the \*\*\*thiol\*\*\* ester is a hydroxy  
\*\*\*thiol\*\*\*  
ester. In other aspects, a weight ratio of elemental sulfur to  
\*\*\*thiol\*\*\* sulfur in the \*\*\*thiol\*\*\* ester molecules  
ranges from  
0.5 to 32.

SUMM The step of the reacting the \*\*\*thiol\*\*\* ester and the  
oxidizing  
agent can be performed at a temperature ranging from 25.degree.  
C. to  
150.degree. C. The process for producing the cross-linked  
\*\*\*thiol\*\*\*  
ester composition can also include the step of stripping residual  
hydrogen sulfide from the cross-linked \*\*\*thiol\*\*\* ester  
composition  
produced. In another aspect, the reaction of the \*\*\*thiol\*\*\*  
ester  
and the elemental sulfur is catalyzed. In some embodiments, the  
catalyst  
is an amine.

SUMM In another of its aspects, the present invention relates to a  
controlled release fertilizer material comprising a particulate  
plant  
nutrient surrounded by a coating which is the reaction product of  
a  
mixture comprising: (i) a first component selected from an

isocyanate  
and/or an epoxy resin, and (ii) a first active hydrogen-  
containing  
compound selected from the group consisting of a \*\*\*thiol\*\*\*  
ester  
composition; a hydroxy \*\*\*thiol\*\*\* ester composition; a  
cross-linked  
\*\*\*thiol\*\*\* ester composition and mixtures thereof.

SUMM In another of its aspects, the present invention relates to a  
process  
for the production of abrasion resistant polythiourethane and/or  
epoxy  
polymer encapsulated controlled release fertilizer particles by  
incorporating in urethane and/or epoxy polymer forming reaction  
mixture  
a sulfur-containing compound such as one or more of a  
\*\*\*thiol\*\*\*  
ester composition; a hydroxy \*\*\*thiol\*\*\* ester composition; a  
cross-linked \*\*\*thiol\*\*\* ester composition, other sulfur-  
based  
compounds described herein below and mixtures thereof.

SUMM Preferably, for the production of the present polythiourethane  
encapsulated controlled release fertilizer material, a sulfur-  
containing  
compound (e.g., one or more of a \*\*\*thiol\*\*\* ester  
composition; a  
hydroxy \*\*\*thiol\*\*\* ester composition; a cross-linked  
\*\*\*thiol\*\*\*  
ester composition) is used as one of the isocyanate-reactive  
components  
(alone or in combination with other active hydrogen-containing  
compounds). Preferably, the sulfur-containing compound comprises  
a  
sulfur-containing vegetable oil. In one preferred embodiment, the  
sulfur-containing vegetable oil comprises a mercaptanized  
vegetable oil  
(MVO), more preferably as described in more detail herein, even  
more  
preferably an MVO produced by the addition of hydrogen sulfide to  
a  
vegetable oil. In another preferred embodiment, the sulfur-  
containing  
vegetable oil comprises mercapto-hydroxy vegetable oil (MHVO),  
more  
preferably as described in more detail herein, even more  
preferably an  
MHVO produced by the addition of hydrogen sulfide to epoxidized  
vegetable oil. In yet another preferred embodiment, the sulfur  
containing vegetable oil comprises sulfur cross-linked  
mercaptanized  
vegetable oil (CMVO), more preferably as described in more detail  
herein, even more preferably an CMVO produced by the addition of  
elemental sulfur to mercaptanized vegetable oil (MVO).

SUMM Preferably, for the production of epoxy polymer encapsulated  
controlled  
release fertilizer material, a sulfur-containing compound (e.g.,  
one or

more of a \*\*\*thiol\*\*\* ester composition; a hydroxy  
\*\*\*thiol\*\*\*  
ester composition; a cross-linked \*\*\*thiol\*\*\* ester  
composition) is  
used as one of the isocyanate-reactive components (alone or in  
combination with other active hydrogen-containing compounds).  
Preferably, the sulfur-containing compound comprises a sulfur-  
containing  
vegetable oil (e.g., MVO and/or MHVO and/or CMVO) is used as one  
of the  
epoxy resin-reactive components.

DRWD FIG. 1 includes two graphs that compare the NMR's of soybean  
oil, which  
is shown in the top graph, and a \*\*\*thiol\*\*\* containing ester  
produced from soybean oil in accordance with an embodiment of the  
present invention, which is shown in the bottom graph;

DRWD FIG. 2 includes two graphs that compare the NMR's of epoxidized  
soybean  
oil, which is shown in the top graph, and a \*\*\*thiol\*\*\*  
containing  
ester produced from epoxidized soybean oil in accordance with an  
embodiment of the present invention, which is shown in the bottom  
graph;

DRWD FIG. 3 is a gas chromatograph (GC)/mass spectrometer (MS) trace  
of a  
\*\*\*thiol\*\*\* containing ester that was produced from soybean  
oil in  
accordance with an embodiment of the present invention and then  
treated  
by methanolysis;

DRWD FIG. 5 is a GC/MS trace of hydroxy \*\*\*thiol\*\*\* containing  
ester  
produced from epoxidized soybean oil in accordance with an  
embodiment of

the present invention and then treated by methanolysis;  
DETD In this specification, " \*\*\*thiol\*\*\* ester composition"  
refers to an

ester composition that includes " \*\*\*thiol\*\*\* ester  
molecules." The  
\*\*\*thiol\*\*\* ester molecule has at least one \*\*\*thiol\*\*\*  
group and  
at least one ester group within the \*\*\*thiol\*\*\* ester  
molecule.

DETD In this specification, "hydroxy \*\*\*thiol\*\*\* ester  
composition"  
refers to an ester composition that includes "hydroxy  
\*\*\*thiol\*\*\*

ester molecules." The hydroxy \*\*\*thiol\*\*\* ester molecule has  
at  
least one \*\*\*thiol\*\*\* group, at least one ester group, and at  
least  
one hydroxy or alcohol group within the hydroxy \*\*\*thiol\*\*\*  
ester  
molecule. Alternatively, the alcohol group and the \*\*\*thiol\*\*\*  
group  
can be combined in the same group, which is referred to as an  
".alpha.-hydroxy \*\*\*thiol\*\*\* group."

DETD In this specification, "polythiourethane" refers to a urethane  
composition that includes more than one of the following

structure:  
 ##STR1## The presence of the thiourethane group can be determined by method known to those skilled in the art (for example infrared spectroscopy, Raman spectroscopy, and/or NMR). \*\*\*Thiol\*\*\*

Ester Composition

DETD The present invention advantageously provides a \*\*\*thiol\*\*\* ester composition as an embodiment of the present invention. The \*\*\*thiol\*\*\* ester composition includes \*\*\*thiol\*\*\* ester molecules that have an average of at least 1.5 ester groups and an average of at least 1.5 \*\*\*thiol\*\*\* groups per \*\*\*thiol\*\*\* ester molecule. The \*\*\*thiol\*\*\* ester composition also has a molar ratio of cyclic sulfides to \*\*\*thiol\*\*\* groups of less than 1.5, as described herein.

DETD Generally, the \*\*\*thiol\*\*\* ester composition contains molecules having at least one ester group and at least one \*\*\*thiol\*\*\* group. The \*\*\*thiol\*\*\* ester composition of this invention can be produced from any unsaturated ester, as described herein. Because the feedstock unsaturated esters can contain multiple carbon-carbon double bonds per unsaturated ester molecule, carbon-carbon double bond reactivity and statistical probability dictate that each \*\*\*thiol\*\*\* ester molecule of the \*\*\*thiol\*\*\* ester composition produced from the unsaturated ester composition will not have the same number of \*\*\*thiol\*\*\* groups, number of unreacted carbon-carbon double bonds, number of cyclic sulfides, molar ratio of carbon-carbon double bonds to \*\*\*thiol\*\*\* groups, molar ratio of cyclic sulfides to \*\*\*thiol\*\*\* groups and other quantities of functional groups and molar ratios disclosed herein as the feedstock unsaturated ester. Additionally, the feedstock unsaturated esters can also comprise a mixture of individual unsaturated esters having a different number of carbon-carbon double bonds and/or ester groups. Thus, many of these properties will be discussed as an average number of the groups per \*\*\*thiol\*\*\* ester molecule within the \*\*\*thiol\*\*\* ester composition or average ratio per \*\*\*thiol\*\*\* ester molecule within the \*\*\*thiol\*\*\* ester composition. In other embodiments, it is desired to control the content of \*\*\*thiol\*\*\*



sulfur present in the \*\*\*thiol\*\*\* ester. Because it is difficult to ensure that the hydrogen sulfide reacts with every carbon-carbon double bond within the unsaturated ester, certain molecules of \*\*\*thiol\*\*\* ester can have more or less \*\*\*thiol\*\*\* groups than other molecules. Thus, the weight percent of \*\*\*thiol\*\*\* groups is stated as an average across all \*\*\*thiol\*\*\* ester molecules of the \*\*\*thiol\*\*\* ester composition.

DETD The \*\*\*thiol\*\*\* ester can be derived from any unsaturated ester described herein.

DETD The \*\*\*thiol\*\*\* ester compositions can be described as comprising one or more separate or discreet functional groups of the \*\*\*thiol\*\*\* ester molecule and/or \*\*\*thiol\*\*\* ester composition. These independent functional groups can include: the number of (or average number of) ester groups per \*\*\*thiol\*\*\* ester molecule, \*\*\*thiol\*\*\* containing the number of (or average number of) \*\*\*thiol\*\*\* groups per \*\*\*thiol\*\*\* ester molecule, the number of (or average number of) unreacted carbon-carbon double bonds per \*\*\*thiol\*\*\* ester molecule, the average \*\*\*thiol\*\*\* sulfur content of the \*\*\*thiol\*\*\* ester composition, the percentage (or average percentage) of sulfide linkages per \*\*\*thiol\*\*\* ester molecule, and the percentage (or average percentage) of cyclic sulfide groups per \*\*\*thiol\*\*\* ester molecule. Additionally, the \*\*\*thiol\*\*\* ester compositions can be described using individual or a combination of ratios including the ratio of double bonds to \*\*\*thiol\*\*\* groups, the ratio of cyclic sulfides to \*\*\*mercaptan\*\*\* group, and the like.

As separate elements, these functional groups of the \*\*\*thiol\*\*\* composition will be described separately.

DETD Minimally, in some embodiments, the \*\*\*thiol\*\*\* ester contains \*\*\*thiol\*\*\* ester molecules having at least one ester group and one \*\*\*thiol\*\*\* group per \*\*\*thiol\*\*\* ester molecule. As the \*\*\*thiol\*\*\* ester is prepared from unsaturated esters, the \*\*\*thiol\*\*\* ester can contain the same number of ester groups as the unsaturated esters described herein. In an embodiment, the \*\*\*thiol\*\*\* ester molecules have an average of at least 1.5 ester groups per \*\*\*thiol\*\*\* ester molecule. Alternatively, the \*\*\*thiol\*\*\* ester

molecules have an average of at least 2 ester groups per  
 \*\*\*thiol\*\*\*  
 ester molecule; alternatively, an average of at least 2.5 ester  
 groups  
 per \*\*\*thiol\*\*\* ester molecule; or alternatively, an average  
 of at  
 least 3 ester groups per \*\*\*thiol\*\*\* ester molecule. In other  
 embodiments, the \*\*\*thiol\*\*\* esters have an average of from  
 1.5 to 8  
 ester groups per \*\*\*thiol\*\*\* ester molecule; alternatively,  
 an  
 average of from 2 to 7 ester groups per \*\*\*thiol\*\*\* ester  
 molecule;  
 alternatively, an average of from 2.5 to 5 ester groups per  
 \*\*\*thiol\*\*\* ester molecule; or alternatively, an average of  
 from 3 to  
 4 ester groups per \*\*\*thiol\*\*\* ester molecule. In yet other  
 embodiments, the \*\*\*thiol\*\*\* ester comprises an average of 3  
 ester  
 groups per \*\*\*thiol\*\*\* ester molecule or alternatively, an  
 average  
 of 4 ester groups per unsaturated ester molecule.  
 DETD Minimally, the \*\*\*thiol\*\*\* ester comprises an average of at  
 least  
 one \*\*\*thiol\*\*\* group per \*\*\*thiol\*\*\* ester molecule. In  
 an  
 embodiment, the \*\*\*thiol\*\*\* ester molecules have an average  
 of at  
 least 1.5 \*\*\*thiol\*\*\* groups per \*\*\*thiol\*\*\* ester  
 molecule;  
 alternatively, \*\*\*thiol\*\*\* containing an average of at least  
 2  
 \*\*\*thiol\*\*\* groups per \*\*\*thiol\*\*\* ester molecule;  
 alternatively,  
 an average of at least 2.5 \*\*\*thiol\*\*\* groups per  
 \*\*\*thiol\*\*\*  
 ester molecule; or alternatively, an average of at least 3  
 \*\*\*thiol\*\*\*  
 groups per \*\*\*thiol\*\*\* ester molecule. In other embodiments,  
 the  
 \*\*\*thiol\*\*\* ester molecules have an average of from 1.5 to 9  
 \*\*\*thiol\*\*\* groups per \*\*\*thiol\*\*\* ester molecule;  
 alternatively,  
 an average of from 3 to 8 \*\*\*thiol\*\*\* groups per  
 \*\*\*thiol\*\*\*  
 ester molecule; alternatively, \*\*\*thiol\*\*\* containing an  
 average of  
 from 2 to 4 \*\*\*thiol\*\*\* groups per \*\*\*thiol\*\*\* ester  
 molecule,  
 or alternatively, an average of from 4 to 8 \*\*\*thiol\*\*\*  
 groups per  
 \*\*\*thiol\*\*\* ester molecule.  
 DETD In other embodiments, the \*\*\*thiol\*\*\* ester can be described  
 by the  
 average amount of \*\*\*thiol\*\*\* sulfur present in \*\*\*thiol\*\*\*  
 ester. In an embodiment, the \*\*\*thiol\*\*\* ester molecules have  
 an  
 average of at least 5 weight percent \*\*\*thiol\*\*\* sulfur per  
 \*\*\*thiol\*\*\* ester molecule; alternatively, an average of at  
 least 10

weight percent \*\*\*thiol\*\*\* sulfur per \*\*\*thiol\*\*\* ester molecule, or alternatively, an average of greater than 15 weight percent \*\*\*thiol\*\*\* sulfur per \*\*\*thiol\*\*\* ester molecule. In an embodiment, the \*\*\*thiol\*\*\* ester molecules have an average of from 5 to 25 weight percent \*\*\*thiol\*\*\* sulfur per \*\*\*thiol\*\*\* ester molecule; alternatively, an average of from 5 to 20 weight percent \*\*\*thiol\*\*\* sulfur per \*\*\*thiol\*\*\* ester molecule; alternatively, an average of from 6 to 15 weight percent \*\*\*thiol\*\*\* sulfur per \*\*\*thiol\*\*\* ester molecule; or alternatively, an average of from 8 to 10 weight percent \*\*\*thiol\*\*\* sulfur per \*\*\*thiol\*\*\* ester molecule.

DETD Generally, the location of the \*\*\*thiol\*\*\* group of the \*\*\*thiol\*\*\* ester is not particularly important and will be dictated by the method used to produce the \*\*\*thiol\*\*\* ester. In embodiments wherein the \*\*\*thiol\*\*\* ester is produced by contacting an unsaturated ester, the position of the \*\*\*thiol\*\*\* group will be dictated by the position of the carbon-carbon double bond. When the carbon-carbon double bond is an internal carbon-carbon double bond, the method of producing the \*\*\*thiol\*\*\* ester will result in a secondary \*\*\*thiol\*\*\* group. However, when the double bond is located at a terminal position it is possible to choose reaction conditions to produce a \*\*\*thiol\*\*\* ester comprising either a primary \*\*\*thiol\*\*\* group or a secondary \*\*\*thiol\*\*\* group.

DETD Some methods of producing the \*\*\*thiol\*\*\* ester composition can additionally create sulfur containing functional groups other than a \*\*\*thiol\*\*\* group. For example, in some \*\*\*thiol\*\*\* ester production methods, an introduced \*\*\*thiol\*\*\* group can react with a carbon-carbon double bond within the same unsaturated ester to produce a sulfide linkage. When the reaction is with a double bond of a second unsaturated ester, this produces a simple sulfide linkage. However, in some instances, the second carbon-carbon double bond is located in the same unsaturated ester molecule. When the \*\*\*thiol\*\*\* group reacts with a second carbon-carbon double bond within the same unsaturated ester molecule, a sulfide linkage is produced. In some instances, the carbon-carbon double bond can be within a second ester group of

the unsaturated ester molecule. While in other instances, the carbon-carbon double bond can be within the same ester group of the unsaturated ester molecule.

DETD When the \*\*\*thiol\*\*\* group reacts with the carbon-carbon double bond in a second ester group of the same unsaturated ester molecule, the cyclic sulfide would contain two ester groups contained within a ring structure. When the \*\*\*thiol\*\*\* group reacts with the carbon-carbon double bond within the same ester group, the cyclic sulfide would not contain an ester group within the ring structure. Within this specification, this second type of cyclic sulfide is referred to as a cyclic sulfide. Within this specification, the first type of sulfide is referred to as a simple sulfide. In the cyclic sulfide case, the sulfide linkage produces a cyclic sulfide functionality within a single ester group of the \*\*\*thiol\*\*\* ester. This linkage is termed a cyclic sulfide for purposes of this application. One such sulfide group that can be produced is a cyclic sulfide. The cyclic sulfide rings that can be produced include a tetrahydrothiopyran ring, a thietane ring, or a thiophane ring (tetrahydrothiophene ring).

DETD In some embodiments, it is desirable to control the average amount of sulfur present as cyclic sulfide in the \*\*\*thiol\*\*\* ester. In an embodiment the average amount of sulfur present as cyclic sulfide in the \*\*\*thiol\*\*\* ester molecules comprises less than 30 mole percent. Alternatively, the average amount of sulfur present as cyclic sulfide in the \*\*\*thiol\*\*\* esters comprises less than 20 mole percent; alternatively, less than 10 mole percent; alternatively, less than 5 mole percent; or alternatively, less than 2 mole percent. In other embodiments, it is desired to control the molar ratio of cyclic sulfides to \*\*\*thiol\*\*\* groups. In other embodiments, it is desirable to have molar ratios of cyclic sulfide to \*\*\*thiol\*\*\* group. In an embodiment, the average molar ratio of cyclic sulfide groups to \*\*\*thiol\*\*\* group per \*\*\*thiol\*\*\* ester is less than 1.5. Alternatively, the average molar ratio of cyclic sulfide groups to \*\*\*thiol\*\*\* group per \*\*\*thiol\*\*\* ester is less than 1; alternatively, less than 0.5; alternatively, less than 0.25; or

alternatively, 0.1. In some embodiments, the ratio of cyclic sulfide groups to \*\*\*thiol\*\*\* group per \*\*\*thiol\*\*\* ester ranges from 0 to 1; or alternatively, the average molar ratio of cyclic sulfide groups to \*\*\*thiol\*\*\* group per \*\*\*thiol\*\*\* ester ranges between 0.05 and 1.

DETD In some instances it can be desirable to have carbon-carbon double bonds present in the \*\*\*thiol\*\*\* ester composition while in other embodiments it can be desirable to minimize the number of carbon-carbon double bonds present in the \*\*\*thiol\*\*\* ester composition.

The presence of carbon-carbon double bonds present in the \*\*\*thiol\*\*\* ester can be stated as an average molar ratio of carbon-carbon double bonds to \*\*\*thiol\*\*\* -sulfur. In an embodiment, the average ratio of the remaining unreacted carbon-carbon double bond in the \*\*\*thiol\*\*\* ester composition to \*\*\*thiol\*\*\* sulfur is less than 1.5 per \*\*\*thiol\*\*\* ester molecule. Alternatively, the average ratio of carbon-carbon double bond to \*\*\*thiol\*\*\* sulfur is less than 1.2 per \*\*\*thiol\*\*\* ester molecule; alternatively, less than 1.0 per \*\*\*thiol\*\*\* ester molecule; alternatively, less than 0.75 per \*\*\*thiol\*\*\* ester molecule; alternatively, less than 0.5 per \*\*\*thiol\*\*\* ester molecule; alternatively, less than 0.2 per \*\*\*thiol\*\*\* ester molecule; or alternatively, less than 0.1

per \*\*\*thiol\*\*\* ester molecule.  
DETD In particular embodiments, the \*\*\*thiol\*\*\* ester is produced from unsaturated ester compositions. Because the feedstock unsaturated ester has particular compositions having a certain number of ester groups present, the product \*\*\*thiol\*\*\* ester composition will have about the same number of ester groups per \*\*\*thiol\*\*\* ester molecule as the feedstock unsaturated ester. Other, independent \*\*\*thiol\*\*\* ester properties described herein can be used to further describe the \*\*\*thiol\*\*\* ester composition.

DETD In some embodiments, the \*\*\*thiol\*\*\* ester molecules are produced from unsaturated esters having an average of less than 25 weight percent of side chains having 3 contiguous methylene interrupted carbon-carbon double bonds, as described herein. In some embodiments, greater than 40 percent of the \*\*\*thiol\*\*\* containing natural source total side

chains can include sulfur. In some embodiments, greater than 60 percent of the \*\*\*thiol\*\*\* ester molecule total side chains can include sulfur. In other embodiments, greater than 50, 70, or 80 percent of the \*\*\*thiol\*\*\* ester molecule total side chains can include sulfur.

DETD In an embodiment, the \*\*\*thiol\*\*\* ester is a \*\*\*thiol\*\*\* containing natural source oil, as described herein. When the \*\*\*thiol\*\*\* ester is a \*\*\*thiol\*\*\* containing natural source oil, functional groups that are present in the \*\*\*thiol\*\*\* containing natural source oil can be described in a "per \*\*\*thiol\*\*\* ester molecule" basis or in a "per triglyceride" basis. The \*\*\*thiol\*\*\* containing natural source oil can have substantially the same properties as the \*\*\*thiol\*\*\* ester composition, such as the molar ratios and other independent descriptive elements described herein.

DETD The average number of \*\*\*thiol\*\*\* groups per triglyceride in the \*\*\*thiol\*\*\* containing natural source oil is greater than about 1.5.

In some embodiments, the average number of \*\*\*thiol\*\*\* groups per triglyceride can range from about 1.5 to about 9.

DETD The \*\*\*thiol\*\*\* ester compositions can also be described as a product produced by the process comprising contacting hydrogen sulfide and an unsaturated ester composition and can be further limited by the process as described herein. The \*\*\*thiol\*\*\* containing natural source oil can also be described using a molecular weight or an average molecular weight of the side chains.

DETD Hydroxy \*\*\*Thiol\*\*\* Ester Composition

DETD In embodiments of the present invention, the \*\*\*thiol\*\*\* ester compositions can also contain a hydroxy or alcohol group. When the \*\*\*thiol\*\*\* ester composition includes the hydroxy group, the \*\*\*thiol\*\*\* ester composition is referred to herein as the hydroxy \*\*\*thiol\*\*\* ester composition. The quantity or number of alcohol groups present in the hydroxy \*\*\*thiol\*\*\* ester composition can be independent of the quantity of other functional groups present in the hydroxy \*\*\*thiol\*\*\* ester composition (i.e. \*\*\*thiol\*\*\* ester groups, sulfides, cyclic sulfides). Additionally, the weight percent of \*\*\*thiol\*\*\* sulfur and functional group ratios

(i.e. molar ratio of cyclic sulfides to \*\*\*thiol\*\*\* groups, molar ratio of \*\*\*epoxide\*\*\* groups to \*\*\*thiol\*\*\* groups, molar ratio of \*\*\*epoxide\*\*\* groups to .alpha.-hydroxy \*\*\*thiol\*\*\* groups and other disclosed quantities of functional groups and their molar ratios to the \*\*\*thiol\*\*\* groups) are separate or discreet elements that can be used to describe the hydroxy \*\*\*thiol\*\*\* ester composition. The hydroxy \*\*\*thiol\*\*\* ester composition can be described using any combination of the hydroxy \*\*\*thiol\*\*\* ester composition separate functional groups or ratios described herein.

DETD In an embodiment, the hydroxy \*\*\*thiol\*\*\* ester composition is produced by reacting hydrogen sulfide with an epoxidized unsaturated ester composition as described herein. Because the epoxidized unsaturated ester can contain multiple \*\*\*epoxide\*\*\* groups, \*\*\*epoxide\*\*\* group reactivity and statistical probability dictate that not all hydroxy \*\*\*thiol\*\*\* ester molecules of the hydroxy \*\*\*thiol\*\*\* ester composition will have the same number of hydroxy groups, \*\*\*thiol\*\*\* groups, .alpha.-hydroxy \*\*\*thiol\*\*\* groups, sulfides, cyclic sulfides, molar ratio of cyclic sulfides to \*\*\*thiol\*\*\* groups, molar ratio of \*\*\*epoxide\*\*\* groups to \*\*\*thiol\*\*\* groups, molar ratio of \*\*\*epoxide\*\*\* groups to .alpha.-hydroxy \*\*\*thiol\*\*\* groups, weight percent \*\*\*thiol\*\*\* sulfur and other disclosed quantities of functional groups and their molar ratios as the epoxidized unsaturated ester composition. Thus, many of these properties will be discussed as an average number or ratio per hydroxy \*\*\*thiol\*\*\* ester molecule. In other embodiments, it is desired to control the content of \*\*\*thiol\*\*\* sulfur present in the hydroxy \*\*\*thiol\*\*\* ester. Because it is difficult to ensure that the hydrogen sulfide reacts with every \*\*\*epoxide\*\*\* group within the epoxidized unsaturated ester, certain hydroxy \*\*\*thiol\*\*\* ester molecules can have more or less \*\*\*thiol\*\*\* groups than other molecules within the hydroxy \*\*\*thiol\*\*\* ester composition. Thus, the weight percent of \*\*\*thiol\*\*\* groups can be stated as an average

weight percent across all hydroxy \*\*\*thiol\*\*\* ester molecules.

DETD As an embodiment of the present invention, the hydroxy \*\*\*thiol\*\*\* ester composition includes hydroxy \*\*\*thiol\*\*\* ester molecules that have an average of at least 1 ester groups and an average of at least 1 .alpha.-hydroxy \*\*\*thiol\*\*\* groups per hydroxy \*\*\*thiol\*\*\* ester molecule. As an embodiment of the present invention, the hydroxy \*\*\*thiol\*\*\* ester composition includes hydroxy \*\*\*thiol\*\*\* ester molecules that have an average of at least 1.5 ester groups and an average of at least 1.5 .alpha.-hydroxy \*\*\*thiol\*\*\* groups per hydroxy \*\*\*thiol\*\*\* ester molecule.

DETD Minimally, in some embodiments, the hydroxy \*\*\*thiol\*\*\* ester comprises at least one ester, at least one \*\*\*thiol\*\*\* group, and at least one hydroxy group. Because the hydroxy \*\*\*thiol\*\*\* ester is prepared from epoxidized unsaturated esters, the hydroxy \*\*\*thiol\*\*\* ester can contain the same number of ester groups as the epoxidized unsaturated esters. In an embodiment, the hydroxy \*\*\*thiol\*\*\* ester molecules have an average of at least 1.5 ester groups per hydroxy \*\*\*thiol\*\*\* ester molecule. Alternatively, the hydroxy \*\*\*thiol\*\*\* ester molecules have an average of at least 2 ester groups per hydroxy \*\*\*thiol\*\*\* ester molecule; alternatively, an average of at least 2.5 ester groups per hydroxy \*\*\*thiol\*\*\* ester molecule; or alternatively, an average of at least 3 ester groups per hydroxy \*\*\*thiol\*\*\* ester molecule. In other embodiments, the hydroxy \*\*\*thiol\*\*\* esters have an average of from 1.5 to 8 ester groups per hydroxy \*\*\*thiol\*\*\* ester molecule; alternatively, an average of from 2 to 7 ester groups per hydroxy \*\*\*thiol\*\*\* ester molecule; alternatively, an average of from 2.5 to 5 ester groups per hydroxy \*\*\*thiol\*\*\* ester molecule; or alternatively, an average of from 3 to 4 ester groups per hydroxy \*\*\*thiol\*\*\* ester molecule. In yet other embodiments, the .alpha.-hydroxy \*\*\*thiol\*\*\* ester comprises an average of 3 ester groups per hydroxy \*\*\*thiol\*\*\* ester molecule or alternatively, an average of 4 ester groups per hydroxy \*\*\*thiol\*\*\* ester molecule.



DETD In some embodiments, the hydroxy group and the \*\*\*thiol\*\*\*  
 group are combined in the same group, which produces the .alpha.-  
 hydroxy \*\*\*thiol\*\*\* group. In other embodiments, the \*\*\*thiol\*\*\*  
 group and the hydroxy or alcohol group are not in the same group. When this  
 occurs, to produce the hydroxy \*\*\*thiol\*\*\* ester composition,  
 the alcohol group is added independently of the \*\*\*thiol\*\*\*  
 group. For example, as another embodiment of the present invention, the  
 hydroxy \*\*\*thiol\*\*\* ester composition advantageously includes hydroxy  
 \*\*\*thiol\*\*\* ester molecules. The hydroxy \*\*\*thiol\*\*\*  
 ester molecules have an average of at least 1.5 ester groups, an  
 average of at least 1.5 \*\*\*thiol\*\*\* groups, and an average of at least 1.5  
 alcohol groups per hydroxy \*\*\*thiol\*\*\* ester molecule.

DETD Minimally, in some embodiments, the hydroxy \*\*\*thiol\*\*\*  
 ester comprises at least one \*\*\*thiol\*\*\* group per hydroxy  
 \*\*\*thiol\*\*\* ester molecule. In an embodiment, the hydroxy \*\*\*thiol\*\*\*  
 ester molecules have an average of at least 1.5 \*\*\*thiol\*\*\* groups  
 per hydroxy \*\*\*thiol\*\*\* ester molecule; alternatively, an average  
 of at least 2 \*\*\*thiol\*\*\* groups per hydroxy \*\*\*thiol\*\*\* ester  
 molecule; alternatively, an average of at least 2.5 \*\*\*thiol\*\*\*  
 groups per hydroxy \*\*\*thiol\*\*\* ester molecule; or  
 alternatively, an average of at least 3 \*\*\*thiol\*\*\* groups per hydroxy  
 \*\*\*thiol\*\*\* ester molecule. In other embodiments, the hydroxy \*\*\*thiol\*\*\*  
 ester molecules have an average of from 1.5 to 9 \*\*\*thiol\*\*\* groups  
 per hydroxy \*\*\*thiol\*\*\* ester molecule; alternatively, an average  
 of from 3 to 8 \*\*\*thiol\*\*\* groups per hydroxy \*\*\*thiol\*\*\*  
 ester molecule; alternatively, an average of from 2 to 4 \*\*\*thiol\*\*\*  
 groups per hydroxy \*\*\*thiol\*\*\* ester molecule; or  
 alternatively, an average of from 4 to 8 \*\*\*thiol\*\*\* groups per hydroxy  
 \*\*\*thiol\*\*\* ester.

DETD Minimally, in some embodiments, the hydroxy \*\*\*thiol\*\*\*  
 ester composition comprises an average of at least 1 hydroxy or alcohol  
 group per hydroxy \*\*\*thiol\*\*\* ester molecule. In some embodiments,  
 the hydroxy \*\*\*thiol\*\*\* ester composition comprises an average of  
 at least 1.5 hydroxy groups per hydroxy \*\*\*thiol\*\*\* ester

molecule;  
 alternatively, average of at least 2 hydroxy groups per hydroxy  
 \*\*\*thiol\*\*\* ester molecule; alternatively, an average of at  
 least 2.5  
 hydroxy groups per hydroxy \*\*\*thiol\*\*\* ester molecule; or  
 alternatively, an average of at least 3 hydroxy groups per  
 \*\*\*thiol\*\*\*  
 ester molecule. In other embodiments, the \*\*\*thiol\*\*\* ester  
 composition comprises an average of from 1.5 to 9 hydroxy groups  
 per  
 hydroxy \*\*\*thiol\*\*\* ester molecule; alternatively, an average  
 of  
 from 3 to 8 hydroxy groups per hydroxy \*\*\*thiol\*\*\* ester  
 molecule;  
 alternatively, an average of from 2 to 4 hydroxy groups per  
 hydroxy  
 \*\*\*thiol\*\*\* ester molecule; or alternatively, an average of  
 from 4 to  
 8 hydroxy groups per hydroxy \*\*\*thiol\*\*\* ester molecule.  
 DETD In yet other embodiments, the number of hydroxy groups can be  
 stated as  
 an average molar ratio of hydroxy group to \*\*\*thiol\*\*\*  
 groups.  
 Minimally, in some embodiments, the molar ratio of hydroxy groups  
 to  
 \*\*\*thiol\*\*\* groups is at least 0.25. In some embodiments, the  
 molar  
 ratio of hydroxy groups to \*\*\*thiol\*\*\* groups is at least  
 0.5;  
 alternatively, at least 0.75; alternatively, at least 1.0;  
 alternatively, at least 1.25; or alternatively, at least 1.5. In  
 other  
 embodiments, the molar ratio of hydroxy groups to \*\*\*thiol\*\*\*  
 groups  
 ranges from 0.25 to 2.0; alternatively, from 0.5 to 1.5; or  
 alternatively, from 0.75 to 1.25.  
 DETD In embodiments where the hydroxy \*\*\*thiol\*\*\* esters are  
 produced  
 from an epoxidized unsaturated ester, the hydroxy \*\*\*thiol\*\*\*  
 esters  
 can be described as containing ester groups and .alpha.-hydroxy  
 \*\*\*thiol\*\*\* groups. The number of ester groups and the number  
 of  
 .alpha.-hydroxy \*\*\*thiol\*\*\* groups are independent elements  
 and as  
 such the hydroxy \*\*\*thiol\*\*\* esters can be described as  
 having any  
 combination of ester groups and .alpha.-hydroxy \*\*\*thiol\*\*\*  
 groups  
 described herein. Minimally, the hydroxy \*\*\*thiol\*\*\* ester  
 comprises  
 an average of at least 1 .alpha.-hydroxy \*\*\*thiol\*\*\* group  
 per  
 hydroxy \*\*\*thiol\*\*\* ester molecule. In some embodiments, the  
 hydroxy  
 \*\*\*thiol\*\*\* ester composition comprises an average of at  
 least 1.5  
 .alpha.-hydroxy \*\*\*thiol\*\*\* groups per hydroxy \*\*\*thiol\*\*\*  
 ester  
 molecule; alternatively, an average of at least 2 .alpha.-hydroxy

\*\*\*thiol\*\*\* groups per hydroxy \*\*\*thiol\*\*\* ester molecule;  
 alternatively, an average of at least 2.5 .alpha.-hydroxy  
 \*\*\*thiol\*\*\* groups per hydroxy \*\*\*thiol\*\*\* ester molecule; or  
 alternatively, an average of at least 3 .alpha.-hydroxy \*\*\*thiol\*\*\* groups per hydroxy  
 \*\*\*thiol\*\*\* ester molecule. In other embodiments, the hydroxy  
 \*\*\*thiol\*\*\* ester composition comprises an average of from 1.5 to 9 .alpha.-hydroxy  
 \*\*\*thiol\*\*\* groups per hydroxy \*\*\*thiol\*\*\* ester molecule; alternatively, an average of from 3 to 8 .alpha.-hydroxy  
 \*\*\*thiol\*\*\* groups per hydroxy \*\*\*thiol\*\*\* ester molecule;  
 alternatively, an average of from 2 to 4 .alpha.-hydroxy  
 \*\*\*thiol\*\*\* groups per hydroxy \*\*\*thiol\*\*\* ester molecule; or  
 alternatively, an average of from 4 to 8 .alpha.-hydroxy \*\*\*thiol\*\*\* groups per hydroxy  
 \*\*\*thiol\*\*\* ester molecule.  
 DETD The hydroxy \*\*\*thiol\*\*\* esters can be produced by contacting an epoxidized ester derived from an unsaturated ester (i.e., epoxidized unsaturated ester), as described herein. In some instances it can be desirable to have \*\*\*epoxide\*\*\* groups present in the hydroxy \*\*\*thiol\*\*\* ester composition. While in other embodiments, it can be desirable to minimize the number of epoxy groups present in the hydroxy \*\*\*thiol\*\*\* ester composition. Thus, the presence of residual \*\*\*epoxide\*\*\* groups can be another separate functional group used to describe the hydroxy \*\*\*thiol\*\*\* ester.  
 DETD The presence of \*\*\*epoxide\*\*\* groups in the hydroxy \*\*\*thiol\*\*\* ester can be independently described as an average number of \*\*\*epoxide\*\*\* groups per hydroxy \*\*\*thiol\*\*\* ester, a molar ratio of \*\*\*epoxide\*\*\* groups to \*\*\*thiol\*\*\* groups, a molar ratio of \*\*\*epoxide\*\*\* groups to .alpha.-hydroxy \*\*\*thiol\*\*\* groups, or any combination thereof. In some embodiments, the hydroxy \*\*\*thiol\*\*\* ester molecules comprise an average of less than 2 \*\*\*epoxide\*\*\* groups per hydroxy \*\*\*thiol\*\*\* ester molecule, i.e., the hydroxy \*\*\*thiol\*\*\* ester molecules have a molar ratio of \*\*\*epoxide\*\*\* groups to .alpha.-hydroxy \*\*\*thiol\*\*\* groups of less than 2. Alternatively, the hydroxy \*\*\*thiol\*\*\* ester comprises an average of less than 1.5 \*\*\*epoxide\*\*\* groups per hydroxy \*\*\*thiol\*\*\* ester molecule; alternatively, an average of less than 1

\*\*\*epoxide\*\*\*  
 group per hydroxy    \*\*\*thiol\*\*\*    ester molecule; alternatively,  
 an  
 average of less than 0.75    \*\*\*epoxide\*\*\*    groups per hydroxy  
 \*\*\*thiol\*\*\*    ester molecule; or alternatively, an average of  
 less than  
 0.5    \*\*\*epoxide\*\*\*    groups per hydroxy    \*\*\*thiol\*\*\*    ester  
 molecule.  
 In other embodiments, the molar ratio of    \*\*\*epoxide\*\*\*    groups  
 to  
 \*\*\*thiol\*\*\*    groups averages less than 1.5. Alternatively, the  
 molar  
 ratio of    \*\*\*epoxide\*\*\*    groups to    \*\*\*thiol\*\*\*    groups  
 averages  
 less than 1; alternatively, averages less than 0.75;  
 alternatively,  
 averages less than 0.5; alternatively, averages less than 0.25;  
 or  
 alternatively, averages less than 0.1. In yet other embodiments,  
 the  
 molar ratio of    \*\*\*epoxide\*\*\*    groups to .alpha.-hydroxy  
 \*\*\*thiol\*\*\*  
 groups averages less than 1.5. Alternatively, the molar ratio of  
 \*\*\*epoxide\*\*\*    groups to .alpha.-hydroxy    \*\*\*thiol\*\*\*  
 groups  
 averages less than 1; alternatively, averages less than 0.75;  
 alternatively, averages less than 0.5; alternatively, averages  
 less than  
 0.25; or alternatively, averages less than 0.1.  
 DETD    In some embodiments, the hydroxy    \*\*\*thiol\*\*\*    ester  
 composition is  
 substantially free of    \*\*\*epoxide\*\*\*    groups.  
 DETD    In other embodiments, the hydroxy    \*\*\*thiol\*\*\*    ester can be  
 described by the average amount of    \*\*\*thiol\*\*\*    sulfur present  
 in  
 hydroxy    \*\*\*thiol\*\*\*    ester. In an embodiment, the hydroxy  
 \*\*\*thiol\*\*\*    ester molecules have an average of at least 2.5  
 weight  
 percent    \*\*\*thiol\*\*\*    sulfur per hydroxy    \*\*\*thiol\*\*\*    ester  
 molecule; alternatively, an average of at least 5 weight percent  
 \*\*\*thiol\*\*\*    sulfur per hydroxy    \*\*\*thiol\*\*\*    ester  
 molecule;  
 alternatively, an average of at least 10 weight percent  
 \*\*\*thiol\*\*\*  
 sulfur per hydroxy    \*\*\*thiol\*\*\*    ester molecule; or  
 alternatively, an  
 average of greater than 15 weight percent    \*\*\*thiol\*\*\*    sulfur  
 per  
 hydroxy    \*\*\*thiol\*\*\*    ester molecule. In an embodiment, the  
 hydroxy  
 \*\*\*thiol\*\*\*    ester molecules have an average of from 5 to 25  
 weight  
 percent    \*\*\*thiol\*\*\*    sulfur per hydroxy    \*\*\*thiol\*\*\*    ester  
 molecule; alternatively, an average of from 5 to 20 weight  
 percent  
 \*\*\*thiol\*\*\*    sulfur per hydroxy    \*\*\*thiol\*\*\*    ester  
 molecule;  
 alternatively, an average of from 6 to 15 weight percent  
 \*\*\*thiol\*\*\*  
 sulfur per hydroxy    \*\*\*thiol\*\*\*    ester molecule; or

alternatively, an average of from 8 to 10 weight percent \*\*\*thiol\*\*\* sulfur per hydroxy \*\*\*thiol\*\*\* ester molecule.

DETD In some embodiments, at least 20 percent of the total side chains include the .alpha.-hydroxy \*\*\*thiol\*\*\* group. In some embodiments, at least 20 percent of the total side chains include the .alpha.-hydroxy \*\*\*thiol\*\*\* group. In some embodiments, at least 60 percent of the total side chains include the .alpha.-hydroxy \*\*\*thiol\*\*\* group; alternatively, at least 70 percent of the total side chains include the .alpha.-hydroxy \*\*\*thiol\*\*\* group. Yet in other embodiments, at least 80 percent of the total side chains include the .alpha.-hydroxy \*\*\*thiol\*\*\* group.

DETD In some aspects, greater than 20 percent of the hydroxy \*\*\*thiol\*\*\* ester molecule total side chains contain sulfur. In some aspects, greater than 40 percent of the hydroxy \*\*\*thiol\*\*\* ester molecule total side chains contain sulfur. In some aspects, greater than 60 percent of the hydroxy \*\*\*thiol\*\*\* ester molecule total side chains contain sulfur; alternatively, greater than 70 percent of the total side chains contain sulfur; or alternatively, greater than 80 percent of the total side chains contain sulfur.

DETD In particular embodiments, the epoxidized unsaturated ester used in the synthesis of the hydroxy \*\*\*thiol\*\*\* ester is produced from the epoxidized unsaturated ester composition that includes an epoxidized natural source oil. Because the natural source oils have particular compositions regarding the number of ester groups present, the hydroxy \*\*\*thiol\*\*\* ester will have about the same number of ester groups as the feedstock natural source oil. Other independent properties that are described herein can be used to further describe the hydroxy \*\*\*thiol\*\*\* ester.

DETD In other embodiments, the epoxidized unsaturated ester used to produce the hydroxy \*\*\*thiol\*\*\* ester is produced from synthetic (or semi-synthetic) unsaturated ester oils. Because the synthetic ester oils can have particular compositions regarding the number of ester groups present, the hydroxy \*\*\*thiol\*\*\* ester would have about the same number of ester groups as the synthetic ester oil. Other,

independent properties of the unsaturated ester, whether the unsaturated ester includes natural source or synthetic oils, can be used to further describe the hydroxy \*\*\*thiol\*\*\* ester composition.

DETD The hydroxy \*\*\*thiol\*\*\* ester compositions can also be described as a product produced by the process comprising contacting hydrogen sulfide and an epoxidized unsaturated ester composition and can be further limited by the process as described herein. The hydroxy \*\*\*thiol\*\*\* containing natural source oil can also be described using an average molecular weight or an average molecular weight of the side chains.

DETD Cross-Linked \*\*\*Thiol\*\*\* Ester Compositions

DETD In an aspect, the present invention relates to a cross-linked \*\*\*thiol\*\*\* ester composition. Generally, the cross-linked \*\*\*thiol\*\*\* ester molecules are oligomers of \*\*\*thiol\*\*\* esters that are connected together by polysulfide linkages --S.sub.x-- wherein x is an integer greater 1. As the cross-linked \*\*\*thiol\*\*\* ester is described as an oligomer of \*\*\*thiol\*\*\* esters, the \*\*\*thiol\*\*\* esters can be described as the monomer from which the cross-linked \*\*\*thiol\*\*\* esters are produced.

DETD In an aspect, the cross-linked \*\*\*thiol\*\*\* ester composition comprises a \*\*\*thiol\*\*\* ester oligomer having at least two \*\*\*thiol\*\*\* ester monomers connected by a polysulfide linkage having a structure --S.sub.Q--, wherein Q is an integer greater than 1. In an aspect, the polysulfide linkage may be the polysulfide linkage --S.sub.Q--, wherein Q is 2, 3, 4, or mixtures thereof. In other embodiments, Q can be 2; alternatively, 3; or alternatively, 4.

DETD In an aspect, the cross-linked \*\*\*thiol\*\*\* ester composition comprises a \*\*\*thiol\*\*\* ester oligomer having at least 3 \*\*\*thiol\*\*\* ester monomers connected by polysulfide linkages; alternatively, 5 \*\*\*thiol\*\*\* ester monomers connected by polysulfide linkages; alternatively, 7 \*\*\*thiol\*\*\* ester monomers connected by polysulfide linkages; or alternatively, 10 \*\*\*thiol\*\*\* ester monomers connected by polysulfide linkages. In yet other embodiments, the cross-linked \*\*\*thiol\*\*\* ester composition comprises a \*\*\*thiol\*\*\* ester oligomer having from 3 to 20 \*\*\*thiol\*\*\* ester monomers connected by polysulfide linkages; alternatively, from 5 to 15 \*\*\*thiol\*\*\* ester monomers connected by polysulfide linkages; or alternatively, from 7 to 12 \*\*\*thiol\*\*\* ester monomers connected by polysulfide linkages.

DETD In an aspect, the cross-linked \*\*\*thiol\*\*\* ester composition comprises \*\*\*thiol\*\*\* ester monomers and \*\*\*thiol\*\*\* ester oligomers. In some embodiments, the cross-linked \*\*\*thiol\*\*\* ester composition has a combined \*\*\*thiol\*\*\* ester monomer and \*\*\*thiol\*\*\* ester oligomer average molecular weight greater than 2,000. In other embodiments, the cross-linked \*\*\*thiol\*\*\* ester composition has a combined \*\*\*thiol\*\*\* ester monomer and \*\*\*thiol\*\*\* ester oligomer average molecular weight greater than 5,000; or alternatively, greater than 10,000. In yet other embodiments, the cross-linked \*\*\*thiol\*\*\* ester composition has a combined \*\*\*thiol\*\*\* ester monomer and \*\*\*thiol\*\*\* ester oligomer average molecular weight ranging from 2,000 to 20,000; alternatively, from 3,000 to 15,000; or alternatively, from 7,500 to 12,500.

DETD In an aspect, the \*\*\*thiol\*\*\* ester monomers and \*\*\*thiol\*\*\* ester oligomers have a total \*\*\*thiol\*\*\* sulfur content greater than 0.5. In other embodiments, the \*\*\*thiol\*\*\* ester monomers and \*\*\*thiol\*\*\* ester oligomers have a total \*\*\*thiol\*\*\* sulfur content greater than 1; alternatively, greater than 2; alternatively, greater than 4. In yet other embodiments, the \*\*\*thiol\*\*\* ester monomers and the \*\*\*thiol\*\*\* ester oligomers have a total \*\*\*thiol\*\*\* sulfur content from 0.5 to 8; alternatively, from 4 to 8; or alternatively, 0.5 to 4.

DETD In an aspect, the \*\*\*thiol\*\*\* ester monomers and \*\*\*thiol\*\*\* ester oligomers have a total sulfur content greater than 8. In some embodiments, the \*\*\*thiol\*\*\* ester monomers and \*\*\*thiol\*\*\* ester oligomers have a total sulfur content greater than 10; alternatively, greater than 12. In yet other embodiments, the \*\*\*thiol\*\*\* ester monomers and \*\*\*thiol\*\*\* ester oligomers have a total sulfur content ranging from 8 to 15 weight percent; alternatively, from 9 to 14; or alternatively, from 10 to 13.

DETD The cross-linked \*\*\*thiol\*\*\* ester compositions can also be described as a product produced by the process comprising contacting a \*\*\*thiol\*\*\* ester with oxidizing agent and can be further limited by the process as described herein.

DETD The present invention advantageously includes sulfide-containing ester compositions as embodiments of the present invention. Generally, the sulfide-containing ester compositions can be described as containing

molecules having at least one ester group and a least one sulfide group within each molecule. The sulfide-containing esters used in the present invention can be produced by contacting either an unsaturated ester or an epoxidized unsaturated ester with a \*\*\*thiol\*\*\* containing compound as described herein.

DETD The feedstock unsaturated esters can contain multiple carbon-carbon double bonds per unsaturated ester molecule. The carbon-carbon bond reactivity and statistical probability, however, dictate that each sulfide-containing ester molecule of the \*\*\*thiol\*\*\* - containing ester composition produced from the unsaturated ester composition will not have the same number of sulfide groups, number of unreacted carbon-carbon double bonds, molar ratio of carbon-carbon double bonds to sulfide groups, molar ratio of cyclic sulfides to \*\*\*thiol\*\*\* groups and other herein disclosed quantities of functional groups and molar ratios. Additionally, the feedstock unsaturated esters can also comprise a mixture of individual unsaturated esters having a different number of carbon-carbon double bonds and/or ester groups. Many of these properties are discussed herein as an average number of the groups per sulfide-containing ester molecule within the sulfide-containing ester composition or average ratio per \*\*\*thiol\*\*\* -containing ester molecule within the sulfide-containing ester composition.

DETD In embodiments related to the sulfide-containing ester that is produced from an epoxidized unsaturated ester, the feedstock epoxidized unsaturated esters can contain multiple \*\*\*epoxide\*\*\* groups per unsaturated ester molecule. Individual \*\*\*epoxide\*\*\* group reactivity and statistical probability dictate that each sulfide-containing ester molecule of the sulfide-containing ester composition produced from the unsaturated ester composition will not have the same number of sulfide groups, number of unreacted \*\*\*epoxide\*\*\* groups, molar ratio of \*\*\*epoxide\*\*\* groups to sulfide groups, and other herein disclosed quantities of functional groups and molar ratios. Additionally, the feedstock epoxidized unsaturated esters can also comprise a mixture of individual epoxidized unsaturated ester molecules having a different number of \*\*\*epoxide\*\*\* groups and/or ester groups. Thus, many of these properties are described as an average number of the groups per sulfide-containing ester molecules within the sulfide-containing ester composition or



average ratio per \*\*\*thiol\*\*\* -containing ester molecule within the sulfide-containing ester composition.

DETD Minimally, in some embodiments, the sulfide-containing esters comprise at least one ester group per sulfide-containing ester molecule. In some embodiments, the sulfide-containing ester has an average of at least 1.5 ester groups per sulfide-containing ester molecule. Alternatively, the sulfide-containing ester molecules have an average of at least 2 ester groups per sulfide-containing ester molecule; alternatively, an average of at least 2.5 ester groups per sulfide-containing ester molecule; or alternatively, an average of at least 3 ester groups per sulfide-containing ester molecule. In other embodiments, the sulfide-containing esters have an average of from 1.5 to 9 ester groups per sulfide-containing ester molecule; alternatively, an average of from 1.5 to 8 ester groups per sulfide-containing ester molecule; alternatively, an average of from 2 to 8 ester groups per sulfide-containing ester molecule; alternatively, an average of from 2 to 7 ester groups per sulfide-containing ester molecule; alternatively, an average of from 2.5 to 5 ester groups per sulfide-containing ester molecule; alternatively, an average of from 3 to 5 ester groups per sulfide-containing ester molecule; or alternatively, an average of from 3 to 4 ester groups per sulfide-containing ester molecule. In yet other embodiments, the hydroxy \*\*\*thiol\*\*\* -containing ester comprises an average of about 3 ester groups per sulfide-containing ester molecule; or alternatively, an average of about 4 ester groups per sulfide-containing ester molecule.

DETD In some embodiments, R.sup.3 comprises at least one functional group. In one aspect, the functional group is selected from the group consisting of a hydroxy group, a carboxylic acid group, a carboxylic ester group, an amine group, a sulfide group, and a second \*\*\*thiol\*\*\* group. In some aspects, R.sup.3 comprises at least two functional groups. In some aspects, the functional groups are selected from the group consisting of a hydroxy group, carboxylic acid group, a carboxylic ester group, an amine group, a sulfide group, a second \*\*\*thiol\*\*\* group, and mixtures thereof.

DETD The sulfide-containing ester compositions can also be described as a

product produced by the process comprising contacting an unsaturated ester with a \*\*\*mercaptan\*\*\* and can be further limited by the process as described herein. In other embodiments, the sulfide-containing ester composition can also be described as a product produced by a process comprising contacting an epoxidized unsaturated ester with a \*\*\*mercaptan\*\*\* and can be further limited by the process as described herein.

DETD Generally, the thioacrylate ester composition can be described as comprising thioacrylate molecules having at least one ester group in addition to any acrylate or thioacrylate ester groups present in the thioacrylate molecule and at least one thioacrylate group. The ester group(s) that are in addition to any acrylate or thioacrylate ester groups present in the thioacrylate molecule are hereinafter referred to as "supplementary ester group(s)." The thioacrylate ester composition described herein can be produced by contacting an acrylate composition with a \*\*\*thiol\*\*\* -containing ester composition and/or a hydroxy \*\*\*thiol\*\*\* -containing ester composition, both of which are described herein.

DETD The feedstock \*\*\*thiol\*\*\* ester compositions and/or hydroxy \*\*\*thiol\*\*\* ester compositions can comprise a mixture of molecules that have an average quantity of ester groups, \*\*\*thiol\*\*\* groups, hydroxy groups, and other groups and molar ratios described herein. Additionally, individual \*\*\*thiol\*\*\* and hydroxy group reactivity within the \*\*\*thiol\*\*\* -containing ester compositions and/or hydroxy \*\*\*thiol\*\*\* ester compositions and statistical probability dictate that each thioacrylate ester molecule of the thioacrylate ester composition produced may not have the same number of ester groups, thioacrylate groups, acrylate groups, and other herein disclosed quantities of functional groups, moieties, and molar ratios. Thus, many of the properties of the thioacrylate ester molecules within the thioacrylate ester composition are described as using an average number of the groups per thioacrylate ester molecule within the thioacrylate ester composition or as an average ratio per thioacrylate ester molecule within the thioacrylate ester composition.

DETD The thioacrylate ester can also be described as a product produced by the process that includes contacting a \*\*\*thiol\*\*\* -containing ester composition with an acrylate composition and can be further limited by the process described herein. In other embodiments, the thioacrylate ester composition can also be described as a product produced by a process that includes contacting a hydroxy \*\*\*thiol\*\*\* -containing ester composition with an acrylate composition and can be further limited by the process described herein.

DETD The present invention advantageously provides a sulfonic acid-containing ester as an embodiment of the present invention. Generally, the sulfonic acid-containing ester of the present invention includes sulfonic acid-containing ester molecules having at least one ester group and a least one sulfonic acid group. The sulfonic acid-containing ester described herein can be produced by contacting a \*\*\*thiol\*\*\* ester with an oxidizing agent as described herein. Because the feedstock for the production of the sulfonic acid-containing ester can include multiple \*\*\*thiols\*\*\* groups, \*\*\*thiol\*\*\* reactivity and statistical probability dictate that each sulfonic acid-containing ester molecule of the sulfonic acid-containing ester will not have the same number of sulfonic acid groups. Additionally, the feedstock \*\*\*thiol\*\*\* ester can also include a mixture of individual \*\*\*thiol\*\*\* ester molecules having different numbers of \*\*\*thiol\*\*\* groups and/or ester groups. Thus, many of the groups present in the sulfonic acid-containing ester are described herein as an average number of the groups per sulfonic acid-containing ester molecule or an average ratio per sulfonic acid-containing ester molecule within the sulfonic acid-containing ester.

DETD In some embodiments of the present invention, the sulfonic acid ester is substantially free of \*\*\*thiol\*\*\* groups.

DETD The sulfonic acid-containing ester can also be described as a product produced by the process comprising contacting a \*\*\*thiol\*\*\* ester with an oxidizing agent described herein.

DETD Process for Making a \*\*\*Thiol\*\*\* Ester Composition

DETD The present invention advantageously provides processes for producing a \*\*\*thiol\*\*\* ester composition as embodiments of the present invention.

As an embodiment, the present invention advantageously includes a process to produce a \*\*\*thiol\*\*\* ester composition by contacting

hydrogen sulfide and an unsaturated ester composition containing unsaturated esters and reacting the hydrogen sulfide and unsaturated

esters to form or produce the \*\*\*thiol\*\*\* ester composition.

As another embodiment of the present invention, a process to produce the \*\*\*thiol\*\*\* ester composition is advantageously provided. In this

embodiment, the process includes contacting a composition comprising a polyol with a composition comprising a \*\*\*thiol\*\*\* containing carboxylic acid composition and reacting the polyol and \*\*\*thiol\*\*\*

containing carboxylic acid composition to form the \*\*\*thiol\*\*\* ester composition.

DETD In some embodiments of the present invention that include producing

\*\*\*thiol\*\*\* ester compositions, the unsaturated ester composition is a natural source oil. In an aspect, the unsaturated ester composition is

soybean oil or alternatively castor oil. Other suitable types of unsaturated ester compositions are described herein and can be used in

the processes for producing the \*\*\*thiol\*\*\* ester compositions.

DETD \*\*\*Thiol\*\*\* Esters from Unsaturated Esters

DETD As an embodiment of the present invention, the \*\*\*thiol\*\*\* esters

described herein can be produced by a process comprising contacting

hydrogen sulfide and an unsaturated ester composition and reacting

hydrogen sulfide and the unsaturated ester composition to form the \*\*\*thiol\*\*\* ester composition. In one embodiment, the

unsaturated ester composition includes unsaturated esters having an average of at

least 1.5 ester groups and an average of at least 1.5 carbon-carbon

double bonds per unsaturated ester molecule. In this embodiment, the

\*\*\*thiol\*\*\* ester composition includes \*\*\*thiol\*\*\* ester molecules

having a molar ratio of cyclic sulfides to \*\*\*thiol\*\*\* groups of less than 1.5.

DETD The processes for producing the \*\*\*thiol\*\*\* ester composition can

be applied to any of the unsaturated esters described herein and used to

produce any of the \*\*\*thiol\*\*\* esters described herein. The process

for producing the \*\*\*thiol\*\*\* ester composition can also

include any additional process steps or process conditions described herein.

DETD The hydrogen sulfide to molar equivalents of unsaturated ester carbon-carbon double bonds molar ratio utilized in the process to produce the \*\*\*thiol\*\*\* ester composition can be any molar ratio that produces the desired \*\*\*thiol\*\*\* ester. The molar equivalents of unsaturated ester carbon-carbon double bonds is calculated by the equation: 
$$\text{UES GMW} = \frac{\text{UES Mass}}{\text{UES C.dbd.C}}$$
 In this equation, UES GMW is the average gram molecular weight of the unsaturated ester, UES Mass is the mass of the feedstock unsaturated ester, and UES C.dbd.C is the average number of double bonds per unsaturated ester molecule. In some embodiments, the \*\*\*thiol\*\*\* ester molecules have a molar ratio of the hydrogen sulfide to the unsaturated ester carbon-carbon double bonds of greater than 2. In other embodiments, the hydrogen sulfide to unsaturated ester carbon-carbon double bonds molar ratio is greater than 5; alternatively, greater than 10; alternatively, greater than 15; or alternatively, greater than 20. In other embodiments, the hydrogen sulfide to unsaturated ester carbon-carbon double bonds molar ratio can be from 2 to 500; alternatively, from 5 to 200; alternatively, from 10 to 100; or alternatively, from 100 to 200.

DETD When a continuous reactor is used, a feed unsaturated ester weight hourly space velocity ranging from 0.1 to 5 can be used to produce the desired \*\*\*thiol\*\*\* ester. Alternatively, the feed unsaturated ester weight hourly space velocity ranges between 0.1 to 5; alternatively, from 0.1 to 2. Alternatively, the feed unsaturated ester weight hourly space velocity is 0.1; alternatively, the feed unsaturated ester weight hourly space velocity is 0.25; or alternatively, the feed unsaturated ester weight hourly space velocity is 2.

DETD The time required for the reaction of the unsaturated ester and hydrogen sulfide can be any time required to form the described \*\*\*thiol\*\*\* ester. Generally, the time required for the reaction of the unsaturated ester and hydrogen sulfide is at least 5 minutes. In some embodiments, the time required for the reaction of the unsaturated ester and hydrogen sulfide ranges from 5 minutes to 72 hours; alternatively, from 10 minutes to 48 hours; or alternatively, from 15 minutes to 36 hours.

DETD In embodiments, the process to produce the \*\*\*thiol\*\*\* ester further comprises a step to remove excess or residual hydrogen sulfide after reacting the hydrogen sulfide and the unsaturated ester composition. In some embodiments, the \*\*\*thiol\*\*\* ester is vacuum stripped. In some embodiments, the \*\*\*thiol\*\*\* ester is vacuum stripped at a temperature ranging between 25.degree. C. and 250.degree. C.; or alternatively, between 50.degree. C. and 200.degree. C. In other embodiments, the \*\*\*thiol\*\*\* ester is sparged with an inert gas to remove hydrogen sulfide. In some embodiments, the \*\*\*thiol\*\*\* ester is sparged with an inert gas at a temperature between 25.degree. C. and 250.degree. C.; or alternatively, between 50.degree. C. and 200.degree. C. In some aspects, the inert gas is nitrogen. Generally, the stripped or sparged \*\*\*thiol\*\*\* ester comprises less than 0.1 weight percent hydrogen sulfide. In other embodiments, the stripped or sparged \*\*\*thiol\*\*\* ester comprises less than 0.05 weight percent sulfur; alternatively, less than 0.025 weight percent hydrogen sulfide; or alternatively, less than 0.01 weight percent hydrogen sulfide.

DETD The reaction between the unsaturated ester and hydrogen sulfide can be performed at any temperature capable of forming the \*\*\*thiol\*\*\* ester. In some embodiments, the unsaturated ester and hydrogen sulfide can be reacted at a temperature greater than -20.degree. C. In other embodiments, the unsaturated ester and hydrogen sulfide can be reacted at a temperature greater than 0.degree. C.; alternatively, greater than 20.degree. C.; alternatively, greater than 50.degree. C.; alternatively, greater than 80.degree. C.; or alternatively, greater than 100.degree. C. In yet other embodiments, the unsaturated ester and hydrogen sulfide can be reacted at a temperature from -20.degree. C. to 200.degree. C.; alternatively, from 120.degree. C. to 240.degree. C.; alternatively, from 170.degree. C. to 210.degree. C.; alternatively, from 185.degree. C. to 195.degree. C.; alternatively, from 20.degree. C. to 200.degree. C.; alternatively, from 20.degree. C. to 170.degree. C.; or alternatively, from 80.degree. C. to 140.degree. C.

DETD \*\*\*Thiol\*\*\* esters having a low cyclic sulfide content can be produced using the disclosed process. In an aspect, the process

for producing the \*\*\*thiol\*\*\* ester forms or produces a \*\*\*thiol\*\*\* ester having a molar ratio of cyclic sulfide to \*\*\*thiol\*\*\* groups of less than 1.5. Additional cyclic sulfide to \*\*\*thiol\*\*\* groups molar ratios are disclosed herein.

DETD In addition to lower cyclic sulfide content, \*\*\*thiol\*\*\* esters having a low carbon-carbon double bond to \*\*\*thiol\*\*\* group molar ratio can also be produced using the disclosed process. In an aspect, the process described herein produces the \*\*\*thiol\*\*\* ester having a carbon-carbon double bond to \*\*\*thiol\*\*\* group molar ratio of less than 1.5. Additional carbon-carbon double bond to \*\*\*thiol\*\*\* group molar ratios are disclosed herein.

DETD In some aspects, the process described herein produces the \*\*\*thiol\*\*\* ester molecules having an average of greater than 5 weight percent \*\*\*thiol\*\*\* sulfur. Additional \*\*\*thiol\*\*\* sulfur contents are disclosed herein. In other aspects, the process for producing a \*\*\*thiol\*\*\* ester forms a \*\*\*thiol\*\*\* ester having greater than 40 percent of the \*\*\*thiol\*\*\* ester total side chains include sulfur. Other percentages of the \*\*\*thiol\*\*\* ester total side chains that include sulfur are disclosed herein.

DETD In some embodiments, the process for producing a \*\*\*thiol\*\*\* ester composition includes contacting an unsaturated ester and hydrogen sulfide and reacting the unsaturated ester and the hydrogen sulfide to form a \*\*\*thiol\*\*\* ester. The \*\*\*thiol\*\*\* ester comprises \*\*\*thiol\*\*\* ester molecules that have a ratio of cyclic sulfide to \*\*\*thiol\*\*\* groups of less than 1.5.

DETD \*\*\*Thiol\*\*\* Ester from a Polyol and a \*\*\*Thiol\*\*\* Containing Carboxylic Acid Derivative

DETD As another embodiment of the present invention, another process to produce the \*\*\*thiol\*\*\* ester composition is advantageously provided. In this embodiment, the process includes the steps of contacting a composition comprising a polyol with a composition comprising a \*\*\*thiol\*\*\* containing carboxylic acid and/or \*\*\*thiol\*\*\* containing carboxylic acid derivative and reacting the polyol and \*\*\*thiol\*\*\* containing carboxylic acid and/or \*\*\*thiol\*\*\* containing carboxylic acid derivative to produce the \*\*\*thiol\*\*\* ester composition. This process can be applied to any polyol, \*\*\*thiol\*\*\* containing carboxylic acid, or \*\*\*thiol\*\*\*

containing carboxylic acid derivative described herein. The process for producing the \*\*\*thiol\*\*\* ester composition can also include any additional process steps or process conditions described herein. Additionally, the process for producing the \*\*\*thiol\*\*\* ester composition can form any \*\*\*thiol\*\*\* ester described herein.

DETD In some embodiments, the \*\*\*thiol\*\*\* ester composition includes \*\*\*thiol\*\*\* ester molecules that have an average of at least 1.5 ester groups and an average of at least 1.5 \*\*\*thiol\*\*\* groups per \*\*\*thiol\*\*\* ester molecule.

DETD The polyol used to produce the \*\*\*thiol\*\*\* ester by contacting a polyol and a \*\*\*thiol\*\*\* carboxylic acid and/or \*\*\*thiol\*\*\* carboxylic acid equivalent (for example a \*\*\*thiol\*\*\* carboxylic acid methyl ester) can be any polyol or mixture of polyols that can produce the described \*\*\*thiol\*\*\* containing ester.

DETD In one aspect, the polyol used to produce the \*\*\*thiol\*\*\* ester can comprise from 2 to 20 carbon atoms. In other embodiments, the polyol comprises from 2 to 10 carbon atoms; alternatively from 2 to 7 carbon atoms; alternatively from 2 to 5 carbon atoms. In further embodiments, the polyol may be a mixture of polyols having an average of 2 to 20 carbon atoms; alternatively, an average of from 2 to 10 carbon atoms; alternatively, an average of 2 to 7 carbon atoms; alternatively an average of 2 to 5 carbon atoms.

DETD In another aspect, the polyol used to produce the \*\*\*thiol\*\*\* ester can have any number of hydroxy groups needed to produce the \*\*\*thiol\*\*\* ester as described herein. In some embodiments, the polyol has 2 hydroxy groups; alternatively 3 hydroxy groups; alternatively, 4 hydroxy groups; alternatively, 5 hydroxy groups; or alternatively, 6 hydroxy groups. In other embodiments, the polyol comprises at least 2 hydroxy groups; alternatively at least 3 hydroxy groups; alternatively, at least 4 hydroxy groups; or alternatively, at least 5 hydroxy groups; at least 6 hydroxy groups. In yet other embodiments, the polyol comprises from 2 to 8 hydroxy groups; alternatively, from 2 to 4 hydroxy groups; or alternatively from 4 to 8 hydroxy groups.

DETD In further aspects, the polyol used to produce the \*\*\*thiol\*\*\* ester is a mixture of polyols. In an embodiment, the mixture of polyols has an average of at least 1.5 hydroxy groups per polyol molecule. In



other embodiments, the mixture of polyols has an average of at least 2 hydroxy groups per polyol molecule; alternatively, an average of at least 2.5 hydroxy groups per polyol molecule; alternatively, an average of at least 3.0 hydroxy groups per polyol molecule; or alternatively, an average of at least 4 hydroxy groups per polyol molecule. In yet another embodiment, the mixture of polyols has an average of 1.5 to 8 hydroxy groups per polyol molecule; alternatively, an average of 2 to 6 hydroxy groups per polyol molecule; alternatively, an average of 2.5 to 5 hydroxy groups per polyol molecule; alternatively, an average of 3 to 4 hydroxy groups per polyol molecule; alternatively, an average of 2.5 to 3.5 hydroxy groups per polyol molecule; or alternatively, an average of 2.5 to 4.5 hydroxy groups per polyol molecule.

DETD In yet another aspect, the polyol or mixture of polyols used to produce the \*\*\*thiol\*\*\* ester has a molecular weight or average molecular weight less than 500. In other embodiments, the polyol or mixture of polyols have a molecular weight or average molecular weight less than 300; alternatively less than 200; alternatively, less than 150; or alternatively, less than 100.

DETD The \*\*\*thiol\*\*\* carboxylic acid and/or \*\*\*thiol\*\*\* carboxylic acid equivalent used to produce the \*\*\*thiol\*\*\* ester by contacting a polyol and a \*\*\*thiol\*\*\* carboxylic acid and/or \*\*\*thiol\*\*\* carboxylic acid equivalent can be any \*\*\*thiol\*\*\* carboxylic acid mixture comprising \*\*\*thiol\*\*\* carboxylic acids, \*\*\*thiol\*\*\* carboxylic acid equivalent or mixture comprising \*\*\*thiol\*\*\* carboxylic acid equivalents that can produce the described \*\*\*thiol\*\*\* containing ester. When talking about the characteristics \*\*\*thiol\*\*\* carboxylic acid equivalent or \*\*\*thiol\*\*\* carboxylic acid equivalents, properties such as number of carbon atoms, average number of carbon atom, molecular weight or average molecular weight, number of \*\*\*thiol\*\*\* group, and average number of \*\*\*thiol\*\*\* groups, one will understand the these properties will apply to the portion of the \*\*\*thiol\*\*\* carboxylic acid equivalent which adds to the polyol to form the \*\*\*thiol\*\*\* ester.

DETD In an aspect, the \*\*\*thiol\*\*\* carboxylic acid and/or  
\*\*\*thiol\*\*\*  
carboxylic acid equivalent used to produce the \*\*\*thiol\*\*\*  
ester  
comprises from 2 to 28 carbon atoms. In an embodiment, the  
\*\*\*thiol\*\*\*  
carboxylic acid and/or \*\*\*thiol\*\*\* carboxylic acid equivalent  
comprises from 4 to 26 carbon atoms; alternatively, from 8 to 24  
carbon  
atoms; alternatively, from 12 to 24 carbon atoms; or  
alternatively, from  
14 to 20 carbon atoms. In other embodiments, a mixture comprising  
\*\*\*thiol\*\*\* carboxylic acid and/or mixture comprising  
\*\*\*thiol\*\*\*  
carboxylic acid equivalents has an average of 2 to 28 carbon  
atoms per  
carboxylic acid and/or carboxylic acid equivalent; alternatively,  
from 4  
to 26 carbon atoms per carboxylic acid and/or carboxylic acid  
equivalent; alternatively, from 8 to 24 carbon atoms per  
carboxylic acid  
and/or carboxylic acid equivalent; alternatively, from 12 to 24  
carbon  
atoms per carboxylic acid and/or carboxylic acid equivalent; or  
alternatively, from 14 to 20 carbon atoms per carboxylic acid  
and/or  
carboxylic acid equivalent.

DETD In another aspect, the \*\*\*thiol\*\*\* carboxylic acid and/or  
\*\*\*thiol\*\*\* carboxylic acid equivalent used to produce the  
\*\*\*thiol\*\*\* ester has at least 1 \*\*\*thiol\*\*\* group;  
alternatively  
2 \*\*\*thiol\*\*\* groups. In some embodiments, a mixture  
comprising  
\*\*\*thiol\*\*\* carboxylic acid and/or mixture comprising  
\*\*\*thiol\*\*\*  
carboxylic acid equivalents has an average of from 0.5 to 3  
\*\*\*thiol\*\*\* groups per carboxylic acid and/or carboxylic acid  
equivalent; alternatively, an average of from 1 to 2  
\*\*\*thiol\*\*\*  
groups per carboxylic acid and/or carboxylic acid equivalent.

DETD In another aspect, the \*\*\*thiol\*\*\* carboxylic acid and/or  
\*\*\*thiol\*\*\* carboxylic acid equivalent used to produce the  
\*\*\*thiol\*\*\* ester has a molecular weight greater than 100;  
alternatively greater than 180; alternatively greater than 240;  
or  
alternatively greater than 260. In other embodiments, the  
\*\*\*thiol\*\*\*  
carboxylic acid and/or \*\*\*thiol\*\*\* carboxylic acid equivalent  
has a  
molecular weight from 100 to 500; alternatively, from 120 to 420;  
alternatively, from 180 to 420; alternatively, from 240 to 420; a  
mixture or alternatively, from 260 to 360. In some embodiments, a  
mixture comprising \*\*\*thiol\*\*\* carboxylic acid and/or mixture  
comprising \*\*\*thiol\*\*\* carboxylic acid equivalents has an  
average  
molecular weight greater than 100 per carboxylic acid and/or  
carboxylic  
acid equivalent; alternatively greater than 180 per carboxylic  
acid  
and/or carboxylic acid equivalent; alternatively greater than 240

per carboxylic acid and/or carboxylic acid equivalent; or  
alternatively  
greater than 260 per carboxylic acid and/or carboxylic acid  
equivalent.  
In yet other embodiments, the mixture comprising of \*\*\*\*thiol\*\*\*  
carboxylic acid and/or mixture comprising \*\*\*\*thiol\*\*\*  
carboxylic acid equivalents has an average molecular weight from 100 to 500  
per carboxylic acid and/or carboxylic acid equivalent; alternatively,  
from 120 to 420 per carboxylic acid and/or carboxylic acid equivalent;  
alternatively, from 180 to 420 per carboxylic acid and/or  
carboxylic acid equivalent; alternatively, from 240 to 420 per carboxylic  
acid and/or carboxylic acid equivalent; a mixture or alternatively,  
from 260 to 360 per carboxylic acid and/or carboxylic acid equivalent.  
DETD In some aspects, the reaction between the polyol and the  
\*\*\*\*thiol\*\*\* containing carboxylic acid and/or \*\*\*\*thiol\*\*\* containing  
carboxylic acid derivative occurs in the presence of a solvent. In other  
aspects the reaction between the polyol and the \*\*\*\*thiol\*\*\*  
containing carboxylic acid and/or \*\*\*\*thiol\*\*\* containing carboxylic acid  
derivative occurs in the substantial absence of a solvent. In  
aspects wherein the reaction between the polyol and the \*\*\*\*thiol\*\*\*  
containing carboxylic acid and/or \*\*\*\*thiol\*\*\* containing  
carboxylic acid derivative occurs in the presence of a solvent, the solvent  
is selected from the group consisting of an aliphatic hydrocarbon,  
an ether, an aromatic compound, or any combination thereof.  
Generally, the solvent, regardless of its chemical class, can include from 1 to  
20 carbon atoms; or alternatively, from 3 to 10 carbon atoms. When  
the solvent includes the aliphatic hydrocarbon, the aliphatic  
hydrocarbon is butane, isobutane, pentane, hexane, heptane, octane, or any  
mixture thereof. When the solvent includes the aromatic compound, the  
aromatic compound is benzene, toluene, xylene, ethylbenzene, or any  
mixture thereof. When the solvent includes the ether, the ether is  
diethyl ether, dipropyl ether, tetrahydrofuran, and any mixture thereof.  
DETD When a solvent is used for the reaction between the polyol and the  
\*\*\*\*thiol\*\*\* containing carboxylic acid and/or \*\*\*\*thiol\*\*\*  
containing carboxylic acid derivative, the quantity of solvent  
can be

any amount that facilitates the reaction. In some embodiments, the mass of the solvent is less than 30 times the mass of the \*\*\*thiol\*\*\* containing carboxylic acid and/or \*\*\*thiol\*\*\* containing carboxylic acid derivative. In other embodiments, the mass of the solvent is less than 20 times the mass of the unsaturated ester oil; alternatively, less than 15 times the mass of the \*\*\*thiol\*\*\* containing carboxylic acid and/or \*\*\*thiol\*\*\* containing carboxylic acid derivative; alternatively, less than 10 times the mass of the \*\*\*thiol\*\*\* containing carboxylic acid and/or \*\*\*thiol\*\*\* containing carboxylic acid derivative; or alternatively, less than 5 times the mass of the \*\*\*thiol\*\*\* containing carboxylic acid and/or \*\*\*thiol\*\*\* containing carboxylic acid derivative. In other embodiments, the mass of the solvent is from 2 times to 20 times the mass of the \*\*\*thiol\*\*\* containing carboxylic acid and/or \*\*\*thiol\*\*\* containing carboxylic acid derivative; alternatively, from 3 times to 15 times the mass of the \*\*\*thiol\*\*\* containing carboxylic acid and/or \*\*\*thiol\*\*\* containing carboxylic acid derivative, or alternatively, from 5 times to 10 times the mass of the \*\*\*thiol\*\*\* containing carboxylic acid and/or \*\*\*thiol\*\*\* containing carboxylic acid derivative.

DETD The equivalent of \*\*\*thiol\*\*\* containing carboxylic acid and/or \*\*\*thiol\*\*\* containing carboxylic acid derivative carboxylic acid groups to equivalents of polyol hydroxy groups molar ratio (hereinafter "carboxylic acid group to polyol hydroxy group molar ratio") utilized in the process to produce the \*\*\*thiol\*\*\* ester composition can be any carboxylic acid group to polyol hydroxy group molar ratio that produces the desired \*\*\*thiol\*\*\* ester composition. In some embodiments, the carboxylic acid group to polyol hydroxy group molar ratio is greater than 0.4. In other embodiments, the carboxylic acid group to polyol hydroxy group molar ratio is greater than 0.6; alternatively, greater than 0.8; alternatively, greater than 1; or alternatively, greater than 1.1. In other embodiments, the carboxylic acid group to polyol hydroxy group molar ratio can range from 0.4 to 1.3; alternatively, from 0.6 to 1.2, or alternatively, from 0.8 to 1.1.

DETD In some aspects, the reaction between the polyol and the  
\*\*\*thiol\*\*\*  
containing carboxylic acid and/or \*\*\*thiol\*\*\* containing  
carboxylic  
acid derivative is catalyzed. In some embodiments, the catalyst  
is a  
mineral acid, such as sulfuric or phosphoric acid. In other  
embodiments,  
the catalyst is an organic acid. In embodiments, for example, the  
organic acid is methane sulfonic acid or toluene sulfonic acid.  
Other  
suitable types of catalyst will be apparent to those of skill in  
the art  
and are to be considered within the scope of the present  
invention.

DETD The reaction of the polyol and the \*\*\*thiol\*\*\* containing  
carboxylic acid and/or \*\*\*thiol\*\*\* containing carboxylic acid  
derivative can occur in a batch reactor or a continuous reactor,  
as  
described herein. The reaction between the polyol and the  
\*\*\*thiol\*\*\*  
containing carboxylic acid and/or \*\*\*thiol\*\*\* containing  
carboxylic  
acid derivative can be performed at any temperature capable of  
forming  
the \*\*\*thiol\*\*\* ester. In some embodiments, the polyol and  
the  
\*\*\*thiol\*\*\* containing carboxylic acid and/or \*\*\*thiol\*\*\*  
containing carboxylic acid derivative can be reacted at a  
temperature  
greater than 20.degree. C. In other embodiments, the polyol and  
the  
\*\*\*thiol\*\*\* containing carboxylic acid and/or \*\*\*thiol\*\*\*  
containing carboxylic acid derivative can be reacted at a  
temperature  
greater than 50.degree. C.; alternatively, greater than  
75.degree. C.;  
or alternatively, greater than 100.degree. C. In yet other  
embodiments,  
the polyol and the \*\*\*thiol\*\*\* containing carboxylic acid  
and/or  
\*\*\*thiol\*\*\* containing carboxylic acid derivative can be  
reacted at a  
temperature from 20.degree. C. to 250.degree. C.; alternatively,  
from  
50.degree. C. to 200.degree. C.; alternatively, from 75.degree.  
C. to  
175.degree. C.; or alternatively, from 100.degree. C. to  
150.degree. C.

DETD The time required for the reaction of the polyol and the  
\*\*\*thiol\*\*\*  
containing carboxylic acid and/or \*\*\*thiol\*\*\* containing  
carboxylic  
acid derivative can be any time required to form the described  
\*\*\*thiol\*\*\* ester oil. Generally, the reaction time of the  
polyol and  
the \*\*\*thiol\*\*\* containing carboxylic acid and/or  
\*\*\*thiol\*\*\*  
containing carboxylic acid derivative is at least 5 minutes. In  
some

embodiments, the reaction time is at least 30 minutes;  
alternatively, at  
least 1 hour; or alternatively, at least 2 hours. In yet other  
embodiments, the reaction time ranges from 5 minutes to 72 hours;  
alternatively, from 30 minutes to 48 hours; alternatively, from 1  
hour  
minutes to 36 hours; or alternatively, from 2 hours and 24 hours.  
DETD When a continuous reactor is used, a feed polyol weight  
unsaturated  
ester weight hourly space velocity ranging from 0.1 to 5 can be  
used to  
produce the desired \*\*\*thiol\*\*\* ester. Alternatively, the  
feed  
polyol weight hourly space velocity ranges between 0.1 to 5;  
alternatively, from 0.1 to 2. Alternatively, the feed polyol  
ester  
weight hourly space velocity is 0.1; alternatively, the feed  
polyol  
weight hourly space velocity is 0.25; or alternatively, the feed  
polyol  
weight hourly space velocity is 2.  
DETD The reaction between the polyol and the \*\*\*thiol\*\*\*  
containing  
carboxylic acid and/or \*\*\*thiol\*\*\* containing carboxylic acid  
derivative can be performed at any reaction pressure that  
maintains the  
polyol and the \*\*\*thiol\*\*\* containing carboxylic acid and/or  
\*\*\*thiol\*\*\* containing carboxylic acid derivative in a liquid  
state.  
In some embodiments, the reaction between the polyol and the  
\*\*\*thiol\*\*\* containing carboxylic acid and/or \*\*\*thiol\*\*\*  
containing carboxylic acid derivative is performed at a pressure  
ranging  
from 0 psia to 2000 psia. In other embodiments, the reaction  
pressure  
ranges from 0 psia to 1000 psia; alternatively, from 0 psia and  
500  
psia; or alternatively, 0 psia to 300 psia.  
DETD In some embodiments, the process to produce the \*\*\*thiol\*\*\*  
ester  
by reacting a polyol and the \*\*\*thiol\*\*\* containing  
carboxylic acid  
and/or \*\*\*thiol\*\*\* containing carboxylic acid derivative can  
further  
include a step to remove excess or residual polyol, \*\*\*thiol\*\*\*  
containing carboxylic acid, and/or \*\*\*thiol\*\*\* containing  
carboxylic  
acid derivative once the polyol has reacted with the  
\*\*\*thiol\*\*\*  
containing carboxylic acid or \*\*\*thiol\*\*\* containing  
carboxylic acid  
derivative. In some embodiments, the \*\*\*thiol\*\*\* ester is  
vacuum  
stripped. In some embodiments, the \*\*\*thiol\*\*\* ester is  
vacuum  
stripped at a temperature ranging between 25.degree. C. and  
250.degree.  
C.; or alternatively, between 50.degree. C. and 200.degree. C. In  
other  
embodiments, the \*\*\*thiol\*\*\* ester is sparged with an inert

gas to remove excess polyol, \*\*\*thiol\*\*\* containing carboxylic acid, and/or \*\*\*thiol\*\*\* containing carboxylic acid derivative. In some embodiments, the \*\*\*thiol\*\*\* ester is sparged with an inert gas at a temperature between 25.degree. C. and 250.degree. C.; or alternatively, between 50.degree. C. and 200.degree. C. In some aspects, the inert gas is nitrogen. Generally, the stripped or sparged \*\*\*thiol\*\*\* ester comprises less than 5 excess polyol, \*\*\*thiol\*\*\* containing carboxylic acid, or \*\*\*thiol\*\*\* containing carboxylic acid derivative. In other embodiments, the stripped or sparged \*\*\*thiol\*\*\* ester comprises less than 2 weight percent excess polyol, \*\*\*thiol\*\*\* containing carboxylic acid, and/or \*\*\*thiol\*\*\* containing carboxylic acid derivative; alternatively, less than 1 weight percent excess polyol, \*\*\*thiol\*\*\* containing carboxylic acid, and/or \*\*\*thiol\*\*\* containing carboxylic acid derivative; or alternatively, less than 0.5 weight percent excess polyol, \*\*\*thiol\*\*\* containing carboxylic acid, and/or \*\*\*thiol\*\*\* containing carboxylic acid derivative.

DETD Process for Making Hydroxy \*\*\*Thiol\*\*\* Ester Composition

DETD The present invention advantageously provides processes for producing a hydroxy \*\*\*thiol\*\*\* ester as embodiments of the present invention.

As an embodiment, the present invention includes a process to produce the hydroxy \*\*\*thiol\*\*\* ester. The process comprises the steps of contacting hydrogen sulfide and an epoxidized unsaturated ester composition and reacting the hydrogen sulfide and the epoxidized unsaturated ester to form the hydroxy \*\*\*thiol\*\*\* ester. As another embodiment of the present invention, another process to produce the hydroxy \*\*\*thiol\*\*\* ester is provided. In this embodiment, the process comprises the steps of contacting a composition comprising a polyol with a composition comprising an hydroxy \*\*\*thiol\*\*\* containing carboxylic acid or an hydroxy \*\*\*thiol\*\*\* containing carboxylic acid derivative and reacting the polyol and the hydroxy \*\*\*thiol\*\*\* containing carboxylic acid or the hydroxy \*\*\*thiol\*\*\* containing carboxylic acid derivative to form the hydroxy \*\*\*thiol\*\*\* ester.

DETD Hydroxy \*\*\*Thiol\*\*\* Ester from Hydrogen Sulfide and an Epoxidized

#### Unsaturated Ester Composition

DETD As an embodiment of the present invention, the hydroxy  
\*\*\*thiol\*\*\*  
ester composition is produced by a process comprising the steps  
of  
contacting hydrogen sulfide and an epoxidized unsaturated ester  
composition and reacting the hydrogen sulfide and the epoxidized  
unsaturated ester to produce the hydroxy \*\*\*thiol\*\*\* ester  
composition.

DETD In some embodiments, the epoxidized unsaturated ester  
composition  
includes epoxidized unsaturated esters that have an average of at  
least  
1 ester groups and an average of at least 1 \*\*\*epoxide\*\*\*  
groups per  
epoxidized unsaturated ester molecule.

DETD The process for producing or preparing the hydroxy \*\*\*thiol\*\*\*  
ester composition can be applied to any of the epoxidized  
unsaturated  
esters described herein and used to produce any hydroxy  
\*\*\*thiol\*\*\*  
ester described herein. The process for producing the hydroxy  
\*\*\*thiol\*\*\* ester can also include any additional process  
steps or  
process conditions as described herein. Additionally, the process  
for  
producing the hydroxy \*\*\*thiol\*\*\* ester can form any hydroxy  
\*\*\*thiol\*\*\* ester described herein.

DETD In some aspects, the hydroxy \*\*\*thiol\*\*\* ester is produced  
by  
contacting hydrogen sulfide with the epoxidized natural source  
oil under  
the reaction conditions to form the hydroxy \*\*\*thiol\*\*\* ester  
in the  
presence of an optional catalyst. In some embodiments, the  
catalyst can  
be a heterogeneous catalyst or a homogeneous catalyst. Examples  
of  
suitable catalysts are described herein. Additional types of  
suitable  
catalysts will be apparent to those of skill in the art and are  
to be  
considered within the scope of the present invention.

DETD The hydrogen sulfide to molar equivalents of \*\*\*epoxide\*\*\*  
groups  
in the epoxidized unsaturated ester (hereinafter "hydrogen  
sulfide to  
\*\*\*epoxide\*\*\* group molar ratio") utilized in the process to  
produce  
the hydroxy \*\*\*thiol\*\*\* ester can be any hydrogen sulfide to  
\*\*\*epoxide\*\*\* group molar ratio that produces the desired  
hydroxy  
\*\*\*thiol\*\*\* ester. The molar equivalents of epoxidized  
unsaturated  
ester epoxidized groups can be calculated by the equation:  
##EQU2##  
In this equation, EUES GMW is the average gram molecular weight  
of the  
epoxidized unsaturated ester, EUES Mass is the mass of the  
epoxidized



unsaturated ester, and EUES \*\*\*Epoxide\*\*\* is the average number of \*\*\*epoxide\*\*\* groups per epoxidized unsaturated ester molecule. In some embodiments, the hydrogen sulfide to \*\*\*epoxide\*\*\* group molar ratio is greater than 0.2. In other embodiments, the hydrogen sulfide to \*\*\*epoxide\*\*\* group molar ratio is greater than 0.5; alternatively, greater than 1; or alternatively, greater than 2. In other embodiments, the hydrogen sulfide to \*\*\*epoxide\*\*\* group molar ratio ranges from 0.2 to 5; alternatively, from 0.5 to 4; or alternatively, from 0.75 to 3. In some embodiments, the hydrogen sulfide to \*\*\*epoxide\*\*\* group molar ratio is greater than 2. In other embodiments, the hydrogen sulfide to \*\*\*epoxide\*\*\* group molar ratio is greater than 5; alternatively, greater than 10; alternatively, greater than 15; or alternatively, greater than 20. In other embodiments, the hydrogen sulfide to \*\*\*epoxide\*\*\* group molar ratio can be from 0.2 to 500; alternatively, from 0.5 to 400; alternatively, from 1 to 300; alternatively, from 2 to 250; alternatively, 5 to 200; or alternatively, from 10 to 100.

DETD The time required for the reaction of the epoxidized unsaturated ester and hydrogen sulfide can be any time required to form the described hydroxy \*\*\*thiol\*\*\* ester. Generally, the time required for the reaction of the epoxidized unsaturated ester and hydrogen sulfide is at least 15 minutes. In some embodiments, the time required for the reaction of the unsaturated ester and hydrogen sulfide ranges from 15 minutes to 72 hours; alternatively, from 30 minutes to 48 hours; alternatively, from 45 minutes to 36 hours.

DETD In some embodiments, the hydroxy \*\*\*thiol\*\*\* ester composition includes hydroxy \*\*\*thiol\*\*\* ester molecules that have an average of greater than 2.5 weight percent \*\*\*thiol\*\*\* sulfur. In some embodiments, the hydroxy \*\*\*thiol\*\*\* ester composition includes hydroxy \*\*\*thiol\*\*\* ester molecules that have an average of greater than 5 weight percent \*\*\*thiol\*\*\* sulfur. Alternatively, in some embodiments, the hydroxy \*\*\*thiol\*\*\* ester molecules have an average ranging from 8 to 10 weight percent \*\*\*thiol\*\*\* sulfur.

DETD In other aspects, the process producing the hydroxy \*\*\*thiol\*\*\* ester composition includes producing hydroxy \*\*\*thiol\*\*\*

ester molecules having an average of greater than 40 percent of the sulfide-containing ester total side chains comprise a sulfide group. Additional embodiments wherein the hydroxy \*\*\*thiol\*\*\* ester comprises a percentage of sulfide-containing ester total side chains are described herein.

DETD In embodiments, the process to produce the hydroxy \*\*\*thiol\*\*\* ester further comprises a step to remove residual hydrogen sulfide after reacting the hydrogen sulfide and the epoxidized unsaturated ester composition. In some embodiments, the hydroxy \*\*\*thiol\*\*\* ester is vacuum stripped. In some embodiments, the hydroxy \*\*\*thiol\*\*\* ester is vacuum stripped at a temperature ranging between 25.degree. C. and 250.degree. C.; or alternatively, between 50.degree. C. and 200.degree. C. In other embodiments, the hydroxy \*\*\*thiol\*\*\* ester is sparged with an inert gas to remove hydrogen sulfide. In some embodiments, the hydroxy \*\*\*thiol\*\*\* ester is sparged with an inert gas at a temperature between 25.degree. C. and 250.degree. C.; or alternatively, between 50.degree. C. and 200.degree. C. In some aspects, the inert gas is nitrogen. Generally, the stripped or sparged hydroxy \*\*\*thiol\*\*\* ester comprises less than 0.1 weight percent hydrogen sulfide. In other embodiments, the stripped or sparged hydroxy \*\*\*thiol\*\*\* ester comprises less than 0.05 weight percent hydrogen sulfide; alternatively, less than 0.025 weight percent hydrogen sulfide; or alternatively, less than 0.01 weight percent hydrogen sulfide.

DETD The reaction between the hydrogen sulfide and the epoxidized unsaturated ester can be performed at any temperature capable of forming the hydroxy \*\*\*thiol\*\*\* ester. In some embodiments, the epoxidized unsaturated ester and hydrogen sulfide can be reacted at a reaction temperature greater than -20.degree. C. In other embodiments, the reaction temperature is greater than 0.degree. C.; alternatively, greater than 20.degree. C.; alternatively, greater than 50.degree. C.; or alternatively, greater than 80.degree. C. In yet other embodiments, the reaction temperature ranges from -20.degree. C. to 200.degree. C.; alternatively, from 20.degree. C. to 170.degree. C.; or alternatively, from 80.degree. C. to 140.degree. C.

DETD In another aspect, the process to produce a hydroxy

\*\*\*thiol\*\*\*  
 ester produces a hydroxy \*\*\*thiol\*\*\* ester having an  
 \*\*\*epoxide\*\*\*  
 group to \*\*\*thiol\*\*\* group molar ratio less than 3.3. In  
 another  
 aspect, the process to produce a hydroxy \*\*\*thiol\*\*\* ester  
 produces  
 a hydroxy \*\*\*thiol\*\*\* ester having an \*\*\*epoxide\*\*\* group  
 to  
 \*\*\*thiol\*\*\* group molar ratio less than 2. Other hydroxy  
 \*\*\*thiol\*\*\*  
 ester \*\*\*epoxide\*\*\* group to \*\*\*thiol\*\*\* group molar  
 ratios are  
 described herein. Alternatively, the hydroxy \*\*\*thiol\*\*\*  
 ester  
 \*\*\*epoxide\*\*\* group to \*\*\*thiol\*\*\* group molar ratio can  
 be less  
 than 1.5; alternatively, less than 1.0; alternatively, less than  
 0.5;  
 alternatively, less than 0.25; or alternatively, less than 0.1.  
 In other  
 embodiments, the hydroxy \*\*\*thiol\*\*\* ester can be  
 substantially free  
 of \*\*\*epoxide\*\*\* groups.  
 DETD In another aspect, the process to produce hydroxy \*\*\*thiol\*\*\*  
 ester  
 produces a hydroxy \*\*\*thiol\*\*\* ester wherein at least 20  
 percent of  
 the side chains comprise an .alpha.-hydroxy \*\*\*thiol\*\*\*  
 group. Other  
 hydroxy \*\*\*thiol\*\*\* ester embodiments wherein the hydroxy  
 \*\*\*thiol\*\*\* ester contains a percentage of side chains  
 comprising  
 .alpha.-hydroxy \*\*\*thiol\*\*\* groups are described herein.  
 DETD Hydroxy \*\*\*Thiol\*\*\* Ester from a Polyol and a Hydroxy  
 \*\*\*Thiol\*\*\*  
 Containing Carboxylic Acid Derivative  
 DETD As another embodiment of the present invention, another process  
 to  
 prepare the hydroxy \*\*\*thiol\*\*\* ester is advantageously  
 provided. In  
 this embodiment, the process includes the steps of contacting a  
 composition comprising a polyol with a composition comprising a  
 hydroxy  
 \*\*\*thiol\*\*\* containing carboxylic acid and/or \*\*\*thiol\*\*\*  
 containing carboxylic acid derivative and reacting the polyol and  
 hydroxy \*\*\*thiol\*\*\* containing carboxylic acid and/or hydroxy  
 \*\*\*thiol\*\*\* containing carboxylic acid to form a hydroxy  
 \*\*\*thiol\*\*\*  
 ester composition. This process can be applied to any polyol, any  
 hydroxy \*\*\*thiol\*\*\* containing carboxylic acid, or any  
 \*\*\*thiol\*\*\*  
 containing carboxylic acid derivative described herein. The  
 process for  
 producing the hydroxy \*\*\*thiol\*\*\* ester composition can also  
 include  
 any additional process steps or process conditions described  
 herein.  
 Additionally, the process for producing the hydroxy \*\*\*thiol\*\*\*  
 ester composition can form any \*\*\*thiol\*\*\* ester described

herein.

DETD In some embodiments, the hydroxy \*\*\*thiol\*\*\* ester composition includes hydroxy \*\*\*thiol\*\*\* ester molecules that have an average of at least 1 ester groups per hydroxy \*\*\*thiol\*\*\* ester molecule and an average of at least 1 .alpha.-hydroxy \*\*\*thiol\*\*\* groups per hydroxy \*\*\*thiol\*\*\* ester molecule.

DETD The polyol used to produce the hydroxy \*\*\*thiol\*\*\* ester by contacting a polyol and a hydroxy \*\*\*thiol\*\*\* carboxylic acid and/or hydroxy \*\*\*thiol\*\*\* carboxylic acid equivalent (for example a hydroxy \*\*\*thiol\*\*\* carboxylic acid methyl ester) can be any polyol or mixture of polyols that can produce the described \*\*\*thiol\*\*\* containing ester.

DETD In one aspect, the polyol used to produce the hydroxy \*\*\*thiol\*\*\* ester can comprise from 2 to 20 carbon atoms. In other embodiments, the polyol comprises from 2 to 10 carbon atoms; alternatively from 2 to 7 carbon atoms; alternatively from 2 to 5 carbon atoms. In further embodiments, the polyol may be a mixture of polyols having an average of 2 to 20 carbon atoms; alternatively, an average of from 2 to 10 carbon atoms; alternatively, an average of 2 to 7 carbon atoms; alternatively an average of 2 to 5 carbon atoms.

DETD In another aspect, the polyol used to produce the hydroxy \*\*\*thiol\*\*\* ester can have any number of hydroxy groups needed to produce the hydroxy \*\*\*thiol\*\*\* ester as described herein. In some embodiments, the polyol has 2 hydroxy groups; alternatively 3 hydroxy groups; alternatively, 4 hydroxy groups; alternatively, 5 hydroxy groups; or alternatively, 6 hydroxy groups. In other embodiments, the polyol comprises at least 2 hydroxy groups; alternatively at least 3 hydroxy groups; alternatively, at least 4 hydroxy groups; or alternatively, at least 5 hydroxy groups; at least 6 hydroxy groups. In yet other embodiments, the polyol comprises from 2 to 8 hydroxy groups; alternatively, from 2 to 4 hydroxy groups; or alternatively from 4 to 8 hydroxy groups.

DETD In further aspects, the polyol used to produce the hydroxy \*\*\*thiol\*\*\* ester is a mixture of polyols. In an embodiment, the mixture of polyols has an average of at least 1.5 hydroxy groups per polyol molecule. In other embodiments, the mixture of polyols has an average of at least 2 hydroxy groups per polyol molecule; alternatively,

an average of at least 2.5 hydroxy groups per polyol molecule;  
alternatively, an average of at least 3.0 hydroxy groups per  
polyol molecule; or alternatively, an average of at least 4 hydroxy  
groups per polyol molecule. In yet another embodiment, the mixture of  
polyols has an average of 1.5 to 8 hydroxy groups per polyol molecule;  
alternatively, an average of 2 to 6 hydroxy groups per polyol  
molecule; alternatively, an average of 2.5 to 5 hydroxy groups per polyol  
molecule; alternatively, an average of 3 to 4 hydroxy groups per  
polyol molecule; alternatively, an average of 2.5 to 3.5 hydroxy groups  
per polyol molecule; or alternatively, an average of 2.5 to 4.5  
hydroxy groups per polyol molecule.

DETD In yet another aspect, the polyol or mixture of polyols used to  
produce the hydroxy \*\*\*thiol\*\*\* ester has a molecular weight or  
average molecular weight less than 500. In other embodiments, the polyol  
or mixture of polyols have a molecular weight or average molecular  
weight less than 300; alternatively less than 200; alternatively, less  
than 150; or alternatively, less than 100.

DETD The hydroxy \*\*\*thiol\*\*\* carboxylic acid and/or hydroxy  
\*\*\*thiol\*\*\* carboxylic acid equivalent used to produce the  
hydroxy \*\*\*thiol\*\*\* ester by contacting a polyol and a hydroxy  
\*\*\*thiol\*\*\* carboxylic acid and/or hydroxy \*\*\*thiol\*\*\* carboxylic acid  
equivalent can be any hydroxy \*\*\*thiol\*\*\* carboxylic acid  
mixture comprising hydroxy \*\*\*thiol\*\*\* carboxylic acids, hydroxy  
\*\*\*thiol\*\*\* carboxylic acid equivalent or mixture comprising  
hydroxy \*\*\*thiol\*\*\* carboxylic acid equivalents that can produce the  
described hydroxy \*\*\*thiol\*\*\* containing ester. When talking about the  
characteristics hydroxy \*\*\*thiol\*\*\* carboxylic acid  
equivalent or hydroxy \*\*\*thiol\*\*\* carboxylic acid equivalents, properties  
such as number of carbon atoms, average number of carbon atom, molecular  
weight or average molecular weight, number of \*\*\*thiol\*\*\* group, and  
average number of \*\*\*thiol\*\*\* groups, one will understand the  
these properties will apply to the portion of the \*\*\*thiol\*\*\*  
carboxylic acid equivalent which adds to the polyol to form the  
\*\*\*thiol\*\*\* ester.

DETD In an aspect, the hydroxy \*\*\*thiol\*\*\* carboxylic acid and/or  
hydroxy \*\*\*thiol\*\*\* carboxylic acid equivalent used to  
produce the

\*\*\*thiol\*\*\* ester comprises from 2 to 28 carbon atoms. In an embodiment, the hydroxy \*\*\*thiol\*\*\* carboxylic acid and/or hydroxy \*\*\*thiol\*\*\* carboxylic acid equivalents comprises from 4 to 26 carbon atoms; alternatively, from 8 to 24 carbon atoms; alternatively, from 12 to 24 carbon atoms; or alternatively, from 14 to 20 carbon atoms. In other embodiments, a mixture comprising hydroxy \*\*\*thiol\*\*\* carboxylic acids and/or mixture comprising hydroxy \*\*\*thiol\*\*\* carboxylic acid equivalents has an average of 2 to 28 carbon atoms per carboxylic acid and/or carboxylic acid equivalent; alternatively, from 4 to 26 carbon per carboxylic acid and/or carboxylic acid equivalent; alternatively, from 8 to 24 carbon atoms per carboxylic acid and/or carboxylic acid equivalent; alternatively, from 12 to 24 carbon per carboxylic acid and/or carboxylic acid equivalent; or alternatively, from 14 to 20 carbon atoms per carboxylic acid and/or carboxylic acid equivalent.

DETD In another aspect, the hydroxy \*\*\*thiol\*\*\* carboxylic acid and/or hydroxy \*\*\*thiol\*\*\* carboxylic acid equivalent used to produce the \*\*\*thiol\*\*\* ester has at least 1 \*\*\*thiol\*\*\* group, alternatively 2 \*\*\*thiol\*\*\* groups. In some embodiments, a mixture comprising hydroxy \*\*\*thiol\*\*\* carboxylic acids and/or mixture comprising hydroxy \*\*\*thiol\*\*\* carboxylic acid equivalents has an average of from 0.5 to 3 \*\*\*thiol\*\*\* groups per carboxylic acid and/or carboxylic acid equivalent; alternatively, an average of from 1 to 2 \*\*\*thiol\*\*\* groups per carboxylic acid and/or carboxylic acid equivalent.

DETD In another aspect, the hydroxy \*\*\*thiol\*\*\* carboxylic acid and/or hydroxy \*\*\*thiol\*\*\* carboxylic acid equivalent used to produce the \*\*\*thiol\*\*\* ester has at least 1 hydroxy group; alternatively, at least 2 hydroxy groups. In some embodiments, a mixture comprising hydroxy \*\*\*thiol\*\*\* carboxylic acids and/or mixture comprising hydroxy \*\*\*thiol\*\*\* carboxylic acid equivalents has an average of from 0.5 to 3 hydroxy groups per carboxylic acid and/or carboxylic acid equivalent; alternatively, an average of from 1 to 2 hydroxy groups per carboxylic acid and/or carboxylic acid equivalent.

DETD In another aspect, the hydroxy \*\*\*thiol\*\*\* carboxylic acid

and/or hydroxy \*\*\*thiol\*\*\* carboxylic acid equivalent used to produce the hydroxy \*\*\*thiol\*\*\* ester has a molecular weight greater than 100; alternatively greater than 180; alternatively greater than 240; or alternatively greater than 260. In other embodiments, the hydroxy \*\*\*thiol\*\*\* carboxylic acid and/or hydroxy \*\*\*thiol\*\*\* carboxylic acid equivalent has a molecular weight from 100 to 500; alternatively, from 120 to 420; alternatively, from 180 to 420; alternatively, from 240 to 420; a mixture or alternatively, from 260 to 360. In some embodiments, a mixture comprising hydroxy \*\*\*thiol\*\*\* carboxylic acids and/or mixture comprising hydroxy \*\*\*thiol\*\*\* carboxylic acid equivalents has an average molecular weight greater than 100 per carboxylic acid and/or carboxylic acid equivalent; alternatively greater than 180 per carboxylic acid and/or carboxylic acid equivalent; alternatively greater than 240 per carboxylic acid and/or carboxylic acid equivalent; or alternatively greater than 260 per carboxylic acid and/or carboxylic acid equivalent. In yet other embodiments, the mixture comprising hydroxy \*\*\*thiol\*\*\* carboxylic acid and/or mixture comprising hydroxy \*\*\*thiol\*\*\* carboxylic acid equivalents has an average molecular weight from 100 to 500 per carboxylic acid and/or carboxylic acid equivalent; alternatively, from 120 to 420 per carboxylic acid and/or carboxylic acid equivalent; alternatively, from 180 to 420 per carboxylic acid and/or carboxylic acid equivalent; alternatively, from 240 to 420 per carboxylic acid and/or carboxylic acid equivalent; a mixture or alternatively, from 260 to 360 per carboxylic acid and/or carboxylic acid equivalent.

DETD In some aspects, the reaction between the polyol and the hydroxy \*\*\*thiol\*\*\* containing carboxylic acid and/or hydroxy \*\*\*thiol\*\*\* containing carboxylic acid derivative occurs in the presence of a solvent. In other aspects, the reaction between the polyol and the hydroxy \*\*\*thiol\*\*\* containing carboxylic acid and/or hydroxy \*\*\*thiol\*\*\* containing carboxylic acid derivative occurs in the substantial absence of a solvent. In aspects wherein the reaction between the polyol and the hydroxy \*\*\*thiol\*\*\* containing carboxylic acid and/or hydroxy \*\*\*thiol\*\*\* containing carboxylic acid derivative occurs in the presence of a solvent, the solvent is selected from the group consisting of an aliphatic hydrocarbon, an ether, an aromatic compound, or any combination thereof. Generally, the

solvent,  
 regardless of its chemical class, includes from 1 to 20 carbon  
 atoms;  
 alternatively, from 3 to 10 carbon atoms. When the solvent  
 includes the  
 aliphatic hydrocarbon, the aliphatic hydrocarbon is butane,  
 isobutane,  
 pentane, hexane, heptane, octane, or any mixture thereof. When  
 the  
 solvent includes the aromatic compound, the aromatic compound is  
 benzene, toluene, xylene, ethylbenzene, or any mixture thereof.  
 When the  
 solvent includes the ether, the ether is diethyl ether, dipropyl  
 ether,  
 tetrahydrofuran, and any mixture thereof.

DETD When a solvent is used for the reaction between the polyol and  
 the  
 hydroxy \*\*\*thiol\*\*\* containing carboxylic acid and/or hydroxy  
 \*\*\*thiol\*\*\* containing carboxylic acid derivative, the  
 quantity of  
 solvent can be any amount that facilitates the reaction. In some  
 embodiments, the mass of the solvent is less than 30 times the  
 mass of  
 the hydroxy \*\*\*thiol\*\*\* containing carboxylic acid and/or  
 hydroxy  
 \*\*\*thiol\*\*\* containing carboxylic acid derivative. In other  
 embodiments, the mass of the solvent is less than 20 times the  
 mass of  
 the hydroxy \*\*\*thiol\*\*\* ester; alternatively, less than 15  
 times the  
 mass of the hydroxy \*\*\*thiol\*\*\* containing carboxylic acid  
 and/or  
 hydroxy \*\*\*thiol\*\*\* containing carboxylic acid derivative;  
 alternatively, less than 10 times the mass of the hydroxy  
 \*\*\*thiol\*\*\*  
 containing carboxylic acid and/or hydroxy \*\*\*thiol\*\*\*  
 containing  
 carboxylic acid derivative; or alternatively, less than 5 times  
 the mass  
 of the hydroxy \*\*\*thiol\*\*\* containing carboxylic acid and/or  
 hydroxy  
 \*\*\*thiol\*\*\* containing carboxylic acid derivative. In other  
 embodiments, the mass of the solvent is from 2 times to 20 times  
 the  
 mass of the hydroxy \*\*\*thiol\*\*\* containing carboxylic acid  
 and/or  
 hydroxy \*\*\*thiol\*\*\* containing carboxylic acid derivative;  
 alternatively, from 3 times to 15 times the mass of the hydroxy  
 \*\*\*thiol\*\*\* containing carboxylic acid and/or hydroxy  
 \*\*\*thiol\*\*\*  
 containing carboxylic acid derivative; or alternatively, from 5  
 times to  
 10 times the mass of the hydroxy \*\*\*thiol\*\*\* containing  
 carboxylic  
 acid and/or hydroxy \*\*\*thiol\*\*\* containing carboxylic acid  
 derivative.

DETD The equivalents of hydroxy \*\*\*thiol\*\*\* containing carboxylic  
 acid  
 derivative and/or hydroxy \*\*\*thiol\*\*\* containing carboxylic  
 acid



derivative carboxylic acid groups to equivalents of polyol hydroxy groups molar ratio (hereinafter referred to as "carboxylic acid group to polyol hydroxy group molar ratio") utilized in the process to produce the hydroxy \*\*\*thiol\*\*\* ester can be any carboxylic acid group to polyol hydroxy group molar ratio that produces the desired hydroxy \*\*\*thiol\*\*\* ester. In some embodiments, the carboxylic acid group to polyol hydroxy group molar ratio is greater than 0.4. In other embodiments, the carboxylic acid group to polyol hydroxy group molar ratio is greater than 0.6; alternatively, greater than 0.8; alternatively, greater than 1; or alternatively, greater than 1.1. In other embodiments, the carboxylic acid group to polyol hydroxy group molar ratio ranges from 0.4 to 1.3; alternatively, from 0.6 to 1.2, or alternatively, from 0.8 to 1.1.

DETD In some aspects, the reaction between the polyol and the hydroxy \*\*\*thiol\*\*\* containing carboxylic acid and/or hydroxy \*\*\*thiol\*\*\* containing carboxylic acid derivative is catalyzed. In some embodiments, the catalyst is a mineral acid, such as sulfuric or phosphoric acid. In other embodiments, the catalyst is an organic acid. In embodiments, for example, the organic acid is methane sulfonic acid or toluene sulfonic acid. Other suitable types of catalyst will be apparent to those of skill in the art and are to be considered within the scope of the present invention.

DETD The reaction of the polyol and the hydroxy \*\*\*thiol\*\*\* containing carboxylic acid and/or hydroxy \*\*\*thiol\*\*\* containing carboxylic acid derivative can occur in a batch reactor or a continuous reactor, as described herein. The reaction between the polyol and the hydroxy \*\*\*thiol\*\*\* containing carboxylic acid and/or hydroxy \*\*\*thiol\*\*\* containing carboxylic acid derivative can be performed at any temperature capable of forming the hydroxy \*\*\*thiol\*\*\* ester.

In some embodiments, the polyol and the hydroxy \*\*\*thiol\*\*\* containing carboxylic acid and/or hydroxy \*\*\*thiol\*\*\* containing carboxylic acid derivative can be reacted at a temperature greater than 20.degree.

C. In other embodiments, the polyol and the hydroxy \*\*\*thiol\*\*\* containing carboxylic acid and/or hydroxy \*\*\*thiol\*\*\* containing carboxylic acid derivative can be reacted at a temperature

greater than 50.degree. C.; alternatively, greater than 75.degree. C.; or alternatively, greater than 100.degree. C. In yet other embodiments, the polyol and the hydroxy \*\*\*thiol\*\*\* containing carboxylic acid and/or hydroxy \*\*\*thiol\*\*\* containing carboxylic acid derivative can be reacted at a temperature from 20.degree. C. to 250.degree. C.; alternatively, from 50.degree. C. to 200.degree. C.; alternatively, from 75.degree. C. to 175.degree. C.; or alternatively, from 100.degree. C. to 150.degree..

DETD The time required for the reaction of the polyol and the hydroxy \*\*\*thiol\*\*\* containing carboxylic acid and/or hydroxy \*\*\*thiol\*\*\* containing carboxylic acid derivative can be any time required to form the described hydroxy \*\*\*thiol\*\*\* ester composition.

Generally, the reaction time is at least 5 minutes. In some embodiments, the reaction time is at least 30 minutes; alternatively, at least 1 hour; or alternatively, at least 2 hours. In yet other embodiments, the reaction time ranges from 5 minutes to 72 hours; alternatively, from 30 minutes to 48 hours; alternatively, from 1 hour minutes to 36 hours; or alternatively, from 2 hours and 24 hours.

DETD The reaction between the polyol and the hydroxy \*\*\*thiol\*\*\* containing carboxylic acid and/or hydroxy \*\*\*thiol\*\*\* containing carboxylic acid derivative can be performed at any reaction pressure that maintains the polyol and the hydroxy \*\*\*thiol\*\*\* containing carboxylic acid and/or hydroxy \*\*\*thiol\*\*\* containing carboxylic acid derivative in a liquid state. In some embodiments, the reaction pressure ranges from 0 psia to 2000 psia. In other embodiments, the reaction pressure ranges from 0 psia to 1000 psia; alternatively, from 0 psia and 500 psia; or alternatively, from 0 psia to 300 psia.

DETD In some embodiments, the process to produce the hydroxy \*\*\*thiol\*\*\* ester composition by reacting a polyol and the hydroxy \*\*\*thiol\*\*\* containing carboxylic acid and/or hydroxy \*\*\*thiol\*\*\* containing carboxylic acid derivative can further include a step to remove excess or residual polyol, hydroxy \*\*\*thiol\*\*\* containing carboxylic acid, and/or hydroxy \*\*\*thiol\*\*\* containing carboxylic acid derivative once the polyol has reacted with the hydroxy \*\*\*thiol\*\*\* containing

carboxylic acid or hydroxy \*\*\*thiol\*\*\* containing carboxylic acid derivative. In some embodiments, the \*\*\*thiol\*\*\* ester is vacuum stripped. In some embodiments, the hydroxy \*\*\*thiol\*\*\* ester is vacuum stripped at a temperature between 25.degree. C. and 250.degree. C.; or alternatively, between 50.degree. C. and 200.degree. C. In other embodiments, the hydroxy \*\*\*thiol\*\*\* ester is sparged with an inert gas to remove excess polyol, hydroxy \*\*\*thiol\*\*\* containing carboxylic acid, and/or hydroxy \*\*\*thiol\*\*\* containing carboxylic acid derivative. In some embodiments, the hydroxy \*\*\*thiol\*\*\* ester is sparged with an inert gas at a temperature between 25.degree. C. and 250.degree. C., or alternatively, between 50.degree. C. and 200.degree. C. In some aspects, the inert gas is nitrogen. Generally, the stripped or sparged hydroxy \*\*\*thiol\*\*\* ester oil comprises less than 5 excess polyol, hydroxy \*\*\*thiol\*\*\* containing carboxylic acid, or hydroxy \*\*\*thiol\*\*\* containing carboxylic acid derivative. In other embodiments, the stripped or sparged hydroxy \*\*\*thiol\*\*\* ester oil comprises less than 2 weight percent excess polyol, hydroxy \*\*\*thiol\*\*\* containing carboxylic acid, and/or hydroxy \*\*\*thiol\*\*\* containing carboxylic acid derivative; less than 1 weight percent excess polyol, hydroxy \*\*\*thiol\*\*\* containing carboxylic acid, and/or hydroxy \*\*\*thiol\*\*\* containing carboxylic acid derivative; or alternatively, less than 0.5 weight percent excess polyol, hydroxy \*\*\*thiol\*\*\* containing carboxylic acid, and/or hydroxy \*\*\*thiol\*\*\* containing carboxylic acid derivative.

DETD A method of making a thioacrylate containing ester composition is advantageously provided as another embodiment of the present invention.

The process for producing the thioacrylate containing ester comprising contacting a \*\*\*thiol\*\*\* ester with an acrylate and converting at least one \*\*\*thiol\*\*\* group to a \*\*\*thiol\*\*\* acrylate group. The process can be applied to any of the \*\*\*thiol\*\*\* esters described herein and used to any thioacrylate ester described herein. The process for producing the thioacrylate ester can also include any additional

process steps or process conditions described herein.

DETD The acrylate compound can be any acrylate compound capable of reacting with a \*\*\*thiol\*\*\* group to form the \*\*\*thiol\*\*\* acrylate group.

In some embodiments, the acrylate compound can be an acrylic halide. In other embodiments, the acrylate compound can be an acrylic acid. In yet other embodiments, the acrylate compound can be an acrylic anhydride.

DETD In some aspects, the conversion of the \*\*\*thiol\*\*\* group to a thioacrylate group occurs in the presence of a solvent. In other aspects the conversion of the \*\*\*thiol\*\*\* group to a thioacrylate group occurs in the substantial absence of a solvent. In aspects wherein the conversion of the \*\*\*thiol\*\*\* group to a thioacrylate group occurs in the presence of a solvent, the solvent may be an aliphatic hydrocarbon, an ether, and aromatic compound. Generally, the solvent, regardless of its chemical class, includes from 1 to 20 carbon atoms; or alternatively, from 3 to 10 carbon atoms. When the solvent includes the aliphatic hydrocarbon, the aliphatic hydrocarbon is butane, isobutane, pentane, hexane, heptane, octane, or any mixture thereof. When the solvent includes the aromatic compound, the aromatic compound is benzene, toluene, xylene, ethylbenzene, or any mixture thereof.

When the solvent includes the ether, the ether is diethyl ether, dipropyl ether, tetrahydrofuran, or any mixture thereof.

DETD When a solvent is used for the conversion of the \*\*\*thiol\*\*\* group to a thioacrylate group, the quantity of solvent can be any amount that facilitates the reaction. In some embodiments, the mass of the solvent is less than 30 times the mass of the \*\*\*thiol\*\*\* ester. In other embodiments, the mass of the solvent is less than 20 times the mass of the \*\*\*thiol\*\*\* ester; alternatively, less than 15 times the mass of the \*\*\*thiol\*\*\* ester; alternatively, less than 10 times the mass of the \*\*\*thiol\*\*\* ester; or alternatively, less than 5 times the mass of the \*\*\*thiol\*\*\* ester. In other embodiments, the mass of the solvent is from 2 times to 20 times the mass of the \*\*\*thiol\*\*\* ester; alternatively, from 3 times to 15 times the mass of the \*\*\*thiol\*\*\* ester; alternatively, 4 times to 15 times the mass of the

the mass        \*\*\*thiol\*\*\*    ester; or alternatively, from 5 times to 10 times

of the        \*\*\*thiol\*\*\*    ester.

DETD    In some aspects the conversion of the        \*\*\*thiol\*\*\*    group to the

thioacrylate group occurs in the presence of a catalyst. In some embodiments, the catalyst is homogeneous. In some embodiments,

the catalyst is an organic amine. Examples of suitable organic amines include triethylamine, tripropylamine, tributylamine, and

pyridine. In other embodiments, the catalyst is heterogeneous. Examples of suitable

catalysts include Amberlyst A-21 and Amberlyst A-26. Other

suitable catalysts will be apparent to those of skill in the art and are to be

considered within the scope of the present invention.

DETD    The conversion of the        \*\*\*thiol\*\*\*    group to a thioacrylate group can

be performed at any conversion temperature that is capable of converting

the        \*\*\*thiol\*\*\*    group to a thioacrylate group. In some embodiments,

the conversion temperature is greater than -20.degree. C. In

other embodiments, the conversion temperature is greater than 0.degree. C.;

alternatively, greater than 20.degree. C.; alternatively, greater than

50.degree. C.; alternatively, greater than 80.degree. C.; or

alternatively, greater than 100.degree. C. In yet other

embodiments, the conversion temperature ranges from -20.degree. C. to 250.degree. C.;

alternatively, from 20.degree. C. to 200.degree. C.; or

alternatively, from 50.degree. C. to 150.degree. C.

DETD    The conversion time required for the conversion of the \*\*\*thiol\*\*\*

group to a thioacrylate group can be any time required to form

the described thioacrylate containing ester. Generally, the conversion time

is at least 5 minutes. In some embodiments, the conversion time

is at least 15 minutes; alternatively, at least 30 minutes;

alternatively, at least 45 minutes; or alternatively, at least 1 hour. In other embodiments, the conversion time ranges from 15 minutes to 12

hours; alternatively, from 30 minutes to 6 hours; or alternatively, from

45 minutes to 3 hours.

DETD    The conversion of the        \*\*\*thiol\*\*\*    group to a thioacrylate group can

be performed at any conversion pressure that maintains the

\*\*\*thiol\*\*\* ester and the acrylate compound in the liquid state. In some embodiments, the conversion pressure ranges from 0 psia to 2000

psia. In other embodiments, the conversion pressure ranges from 0 psia to 1000 psia; or alternatively, from 0 psia to 500 psia.

DETD Process for Producing Cross-Linked \*\*\*Thiol\*\*\* Ester

DETD As an embodiment of the present invention, a process for producing a cross-linked \*\*\*thiol\*\*\* ester composition is advantageously provided. Minimally, in some embodiments, the process to produce the cross-linked \*\*\*thiol\*\*\* ester composition comprises contacting a \*\*\*thiol\*\*\* ester composition with an oxidizing agent and reacting the \*\*\*thiol\*\*\* ester composition and an oxidizing agent to form the \*\*\*thiol\*\*\* ester oligomer having at least two \*\*\*thiol\*\*\* ester monomers connected by a polysulfide linkage having the structure --S.sub.Q--, wherein Q is an integer greater than 1. The disclosed method may be applied to any \*\*\*thiol\*\*\* ester described herein to produce any cross-linked \*\*\*thiol\*\*\* ester composition as described herein. The process to produce the cross-linked \*\*\*thiol\*\*\* ester composition can also include any additional process steps or process conditions as described herein.

DETD When elemental sulfur is used as the oxidizing agent, the quantity of elemental sulfur utilized to form the cross-linked \*\*\*thiol\*\*\* ester composition is determined as a function of the \*\*\*thiol\*\*\* sulfur content of the \*\*\*thiol\*\*\* ester composition. In an aspect, the weight ratio of elemental sulfur to \*\*\*thiol\*\*\* sulfur in the \*\*\*thiol\*\*\* ester composition is at least 0.5. In some embodiments, the weight ratio of elemental sulfur to \*\*\*thiol\*\*\* sulfur in the \*\*\*thiol\*\*\* ester composition is at least 5; alternatively, at least 10, alternatively, at least 15, or alternatively, at least 20. In other embodiments, the weight ratio of elemental sulfur to \*\*\*thiol\*\*\* sulfur in the \*\*\*thiol\*\*\* ester composition ranges from 0.5 to 32; alternatively, ranges from 1 to 24; alternatively, ranges from 2 to 16; or alternatively, ranges from 3 to 10.

DETD In an aspect, the reaction of the \*\*\*thiol\*\*\* ester and elemental sulfur occurs in the presence of a catalyst. The catalyst can be any catalyst that catalyzes the formation of the polysulfide linkage between

at least two \*\*\*thiol\*\*\* ester monomers. In some embodiments, the catalyst is an amine. In further embodiments, the catalyst is a tertiary amine.

DETD The formation of the cross-linked \*\*\*thiol\*\*\* ester can occur in a batch reactor or a continuous reactor, as described herein. The formation of the cross-linked \*\*\*thiol\*\*\* ester can occur at any temperature capable of forming the \*\*\*thiol\*\*\* ester. In some embodiments, the formation of the cross-linked \*\*\*thiol\*\*\* ester can occur at a temperature greater than 25.degree. C. In other embodiments, the formation of the cross-linked \*\*\*thiol\*\*\* ester can occur at a temperature greater than 50.degree. C.; alternatively, greater than 70.degree. C.; or alternatively, greater than 80.degree. C. In yet other embodiments, the formation of the cross-linked \*\*\*thiol\*\*\* ester occurs at a temperature from 25.degree. C. to 150.degree. C.; alternatively, from 50.degree. C. to 150.degree. C.; alternatively, from 70.degree. C. to 120.degree. C.; or alternatively, from 80.degree. C. to 110.degree. C.

DETD The time required to form the cross-linked \*\*\*thiol\*\*\* ester can be any time required to form the desired cross-linked \*\*\*thiol\*\*\* ester. Generally, the time required to form the cross-linked \*\*\*thiol\*\*\* ester is at least 15 minutes. In some embodiments, the time required to form the cross-linked \*\*\*thiol\*\*\* ester is at least 30 minutes; alternatively, at least 1 hour; or alternatively, at least 2 hours. In yet other embodiments, the time required to form the cross-linked \*\*\*thiol\*\*\* ester ranges from 15 minutes to 72 hours; alternatively, from 30 minutes to 48 hours; alternatively, from 1 hour minutes to 36 hours; or alternatively, from 2 hours and 24 hours.

DETD In embodiments, the process to produce the cross-linked \*\*\*thiol\*\*\* ester further comprises a step to remove residual hydrogen sulfide. In some embodiments the cross-linked \*\*\*thiol\*\*\* ester is vacuum stripped. In some embodiments, the cross-linked \*\*\*thiol\*\*\* ester is vacuum striped at a temperature between 25.degree. C. and 250.degree. C.; alternatively, between 50.degree. C. and 200.degree. C.; or alternatively, 75 and 150.degree. C. In some embodiments, the cross-linked \*\*\*thiol\*\*\* ester oil is sparged with an inert gas to remove residual hydrogen sulfide. In other embodiments, the cross-linked

\*\*\*thiol\*\*\* ester is sparged with an inert gas at a temperature between 25.degree. C. and 250.degree. C.; alternatively, between 50.degree. C. and 200.degree. C.; or alternatively, between 75 and 150.degree. C. In yet other embodiments, the vacuum stripping is performed while sparging the cross-linked \*\*\*thiol\*\*\* ester with an inert gas. In yet other embodiments, the vacuum stripping is performed while sparging the cross-linked \*\*\*thiol\*\*\* ester an inert gas at a temperature between 25.degree. C. and 250.degree. C.; alternatively, between 50.degree. C. and 200.degree. C.; or alternatively, 75 and 150.degree. C. In some embodiments, the inert gas is nitrogen.

DETD Generally, the stripped or sparged cross-linked \*\*\*thiol\*\*\* ester comprises less than 0.1 weight percent hydrogen sulfide. In other embodiments, the stripped or sparged \*\*\*thiol\*\*\* -containing ester oil comprises less than 0.05 weight percent hydrogen sulfide; alternatively, less than 0.025 weight percent hydrogen sulfide; or alternatively, less than 0.01 weight percent hydrogen sulfide.

DETD The present invention advantageously provides processes for producing sulfide-containing esters as embodiments of the present invention. Generally, the sulfide-containing esters can be prepared by two processes. As an embodiment of the present invention, the first process used to produce a sulfide-containing ester comprises contacting an unsaturated ester and a \*\*\*mercaptan\*\*\* and reacting the unsaturated ester and \*\*\*mercaptan\*\*\* to form a sulfide-containing ester. As another embodiment of the present invention, the second process used to produce a sulfide-containing ester comprises contacting an epoxidized unsaturated ester and a \*\*\*mercaptan\*\*\* sulfide and reacting the unsaturated ester and \*\*\*mercaptan\*\*\* to form a sulfide-containing ester. Additional aspects of the two sulfide-containing ester production processes are described below.

DETD The sulfide-containing esters and sulfide-containing ester compositions described herein can be produced by a process comprising contacting a \*\*\*mercaptan\*\*\* and an unsaturated ester and reacting the \*\*\*mercaptan\*\*\* and the unsaturated ester to form a sulfide-containing ester. The process can be applied to any of the unsaturated esters and \*\*\*mercaptans\*\*\* described herein. The process for producing



the sulfide-containing ester can also include any additional process steps or process conditions described herein. Additionally, the process for producing the sulfide-containing ester can form any sulfide-containing ester described herein.

DETD In some aspects, the reaction between the \*\*\*mercaptan\*\*\* and the unsaturated ester occurs in the presence of a solvent. In other aspects the reaction between the \*\*\*mercaptan\*\*\* and the unsaturated ester occurs in the substantial absence of a solvent. When the reaction occurs in the presence of a solvent, the solvent is selected from an aliphatic hydrocarbon, an ether, an aromatic compound, an alcohol, or any combination thereof. Generally, the solvent, regardless of its chemical class, can comprise from 1 to 20 carbon atoms; alternatively, from 3 to 10 carbon atoms. When the solvent includes an aliphatic hydrocarbon, the aliphatic hydrocarbon is butane, isobutane, pentane, hexane, heptane, octane, or any mixture thereof. When the solvent includes an aromatic compound, the aromatic compound is benzene, toluene, xylene, ethylbenzene, or any mixture thereof. When the solvent includes an alcohol, the alcohol is methanol, 1-propanol, 2-propanol, 1-butanol, 2-butanol, 2-methyl-2-proanol, or any mixture thereof. When the solvent includes an ether, the ether is diethyl ether, dipropyl ether, tetrahydrofuran, or any mixture thereof.

DETD When a solvent is used for the reaction between the \*\*\*mercaptan\*\*\* and the unsaturated ester, the quantity of solvent can be any amount that facilitates the reaction, as understood by those of skill in the art. In some embodiments, the mass of the solvent is less than 30 times the mass of the unsaturated ester. In other embodiments, the mass of the solvent is less than 20 times the mass of the unsaturated ester; alternatively, less than 15 times the mass of the unsaturated ester; alternatively, less than 10 times the mass of the unsaturated ester; or alternatively, less than 5 times the mass of the unsaturated ester. In other embodiments, the mass of the solvent is from 2 times to 20 times the mass of the unsaturated ester; alternatively, from 3 times to 15 times the mass of the unsaturated ester; alternatively, from 4

times to  
15 times the mass of the unsaturated ester; or alternatively,  
from 5  
times to 10 times the mass of the unsaturated ester.

DETD The molar ratio of \*\*\*mercaptan\*\*\* to molar equivalents of  
unsaturated ester carbon-carbon double bonds (herein after "  
\*\*\*mercaptan\*\*\* to carbon-carbon double bond molar ratio")  
utilized in  
the process to produce the sulfide-containing ester can be any  
\*\*\*mercaptan\*\*\* to carbon-carbon double bond molar ratio that  
produces  
the desired sulfide-containing ester. The molar equivalents of  
unsaturated ester carbon-carbon double bonds is calculated by the  
equation:  $\frac{\text{UES Mass}}{\text{UES C.dbd.C}}$  In this equation, UES GMW is the average  
gram  
molecular weight of the unsaturated ester, UES Mass is the mass  
of the  
unsaturated ester, and UES C.dbd.C is the average number of  
double bonds  
per unsaturated ester molecule. In some embodiments, the  
\*\*\*mercaptan\*\*\* to carbon-carbon double bond molar ratio is  
greater  
than 0.25. In other embodiments, the \*\*\*mercaptan\*\*\* to  
carbon-carbon double bond molar ratio is greater than 0.5;  
alternatively, greater than 0.75; alternatively, greater than 1;  
alternatively, greater than 1.25; or alternatively, greater than  
1.5. In  
other embodiments, the \*\*\*mercaptan\*\*\* to carbon-carbon  
double bond  
molar ratio can range from 0.25 to 2; alternatively, from 0.5 to  
1.5, or  
alternatively, from 0.75 to 1.25.

DETD In some aspects the reaction between the \*\*\*mercaptan\*\*\* and  
the  
unsaturated ester is catalyzed. The reaction of the  
\*\*\*mercaptan\*\*\*  
and the unsaturated ester can be catalyzed by a heterogeneous  
catalyst  
or homogeneous catalyst, as described herein. In some aspects,  
the  
reaction between the \*\*\*mercaptan\*\*\* and the unsaturated  
ester is  
initiated by a free radical initiator or ultraviolet radiation,  
as  
described herein.

DETD The free radical initiator can be any free radical initiator  
capable of  
forming free radicals under thermal or light photolysis.  
Generally, the  
free radical initiator is selected from the general class of  
compounds  
having a --N.dbd.N-- group or a --O-- O-- group. Specific classes  
of  
free radical initiators include diazo compounds, dialkyl  
peroxides,  
hydroperoxides, and peroxy esters. Specific initiators include  
azobenzene, 2,2'-azobis(2-methylpropionitrile,  
4,4'-azobis(4-cyanovaleric acid), 1,1'-azobis(cyclohexanecarbo-  
nitrile),  
2,2'-azobis(2methylpropane), 2,2'-azobis(2-methylpropionamidine)

dihydro-  
chloride, methylpropionitrile, azodicarboxamide, tert-butyl  
hydroperoxide, di-tert-butyl peroxide, octylperbenzoate. In some  
embodiments, the free radical initiated reaction of the  
\*\*\*mercaptan\*\*\* and the unsaturated ester is performed at a  
reaction  
temperature within  $\pm 50$  degree. C. of the 1 hour half life of  
the free  
radical initiator. In other embodiments, the reaction temperature  
is  
within  $\pm 25$  degree. C. of the 1 hour half life of the free  
radical  
initiator; alternatively, the reaction temperature is within  
 $\pm 20$  degree. C. of the 1 hour half life of the free radical  
initiator;  
alternatively, the reaction temperature is within  $\pm 15$  degree.  
C. of  
the 1 hour half life of the free radical initiator; or  
alternatively,  
the reaction temperature is within  $\pm 10$  degree. C. of the 1  
hour half  
life of the free radical initiator. In embodiments where the free  
radical initiated reaction of the \*\*\*mercaptan\*\*\* and the  
unsaturated ester is initiated by light photolysis, the light can  
be any  
light capable creating free radicals. In some embodiments, the  
light is  
UV radiation. Other sources of light capable of creating free  
radicals  
will be apparent to those of skill in the art and are to be  
considered  
within the scope of the present invention.

DETD In another aspect, the reaction of the \*\*\*mercaptan\*\*\* and  
the  
unsaturated ester is initiated by UV radiation. In these  
embodiments,  
the UV radiation may be any UV radiation capable of initiating  
the  
reaction of the \*\*\*mercaptan\*\*\* and the unsaturated ester. In  
some  
embodiments, the UV radiation is generated by a medium pressure  
mercury  
lamp.

DETD The reaction of the \*\*\*mercaptan\*\*\* and the unsaturated  
ester can  
occur in a batch reactor of a continuous reactor. Any of the  
batch or  
continuous reactors described herein can be used in this  
reaction. Other  
suitable reactors will be apparent to those of skill in the art  
and are  
to be considered within the scope of the present invention.

DETD The reaction time for reacting the \*\*\*mercaptan\*\*\* and the  
unsaturated ester can be any time required to form the  
sulfide-containing ester. Generally, the reaction time is at  
least 5  
minutes. In some embodiments, the reaction time ranges from 5  
minutes to  
72 hours; alternatively, from 10 minutes to 48 hours; or  
alternatively,

from 15 minutes to 36 hours.

DETD In some embodiments, the process to produce the sulfide-containing ester further comprises a step to remove any residual \*\*\*mercaptan\*\*\* that remains after reacting the \*\*\*mercaptan\*\*\* and the unsaturated ester. In some embodiments, the sulfide-containing ester is vacuum stripped to remove the residual \*\*\*mercaptan\*\*\*. In some embodiments, the sulfide-containing ester is vacuum stripped at a temperature between 25.degree. C. and 250.degree. C.; or alternatively, between 50.degree. C. and 200.degree. C. In other embodiments, the sulfide-containing ester is sparged with an inert gas to remove the residual \*\*\*mercaptan\*\*\*. In some embodiments, the sulfide-containing ester is sparged with an inert gas at a temperature between 25.degree. C. and 250.degree. C.; or alternatively, between 50.degree. C. and 200.degree. C. In some aspects, the inert gas is nitrogen. Generally, the stripped or sparged sulfide-containing ester comprises less than 5 weight percent of the \*\*\*mercaptan\*\*\*. In other embodiments, the stripped or sparged sulfide-containing ester comprises less than 2 weight percent of the \*\*\*mercaptan\*\*\*; alternatively, less than 1 weight percent of the \*\*\*mercaptan\*\*\*; or alternatively, less than 0.5 weight percent of the \*\*\*mercaptan\*\*\*.

DETD The reaction between the \*\*\*mercaptan\*\*\* and the unsaturated ester can be performed at any temperature capable of forming the sulfide-containing ester. In some embodiments, the \*\*\*mercaptan\*\*\* and the unsaturated ester can be reacted at a reaction temperature of greater than -20.degree. C. In other embodiments, the reaction temperature is greater than 0.degree. C.; alternatively, greater than 20.degree. C.; alternatively, greater than 50.degree. C.; alternatively, greater than 80.degree. C.; or alternatively, greater than 100.degree. C. In yet other embodiments, the \*\*\*mercaptan\*\*\* and the unsaturated ester can be reacted at a temperature from -20.degree. C. to 250.degree. C.; alternatively, from 20.degree. C. to 200.degree. C.; or alternatively, from 80.degree. C. to 160.degree. C.

DETD The reaction between the \*\*\*mercaptan\*\*\* and the unsaturated ester can be performed at any pressure that maintains the \*\*\*mercaptan\*\*\* and the unsaturated ester in a substantially liquid state. In

some embodiments, the \*\*\*mercaptan\*\*\* and the unsaturated ester can be performed at a reaction pressure ranging from 0 psig to 2000 psig. In other embodiments, the reaction pressure ranges from 0 psig to 1000 psig; alternatively, from 0 psig to 500 psig; or alternatively, from 0 psig to 200 psig.

DETD Using the disclosed process, sulfide-containing ester having a low carbon-carbon double bond to sulfide group molar ratio can be produced. In an aspect, the process for producing the sulfide-containing ester forms a sulfide-containing ester having a carbon-carbon double bond to \*\*\*thiol\*\*\* group molar ratio of less than 1.5. Additional carbon-carbon double bond to sulfide group molar ratios are disclosed herein.

DETD As another embodiment of the present invention, another process for producing a class of sulfide-containing esters, which includes hydroxy sulfide-containing esters, is advantageously provided. In this embodiment, the hydroxy sulfide-containing esters and hydroxy sulfide-containing ester compositions can be produced by a process comprising the steps of contacting a \*\*\*mercaptan\*\*\* and an epoxidized unsaturated ester and reacting the \*\*\*mercaptan\*\*\* and the epoxidized unsaturated ester to produce or form the hydroxy sulfide-containing ester. The process can be applied to any \*\*\*mercaptan\*\*\* and/or any epoxidized unsaturated esters described herein. The process for producing the hydroxy sulfide-containing ester can also include any additional process steps or process conditions as described herein. Additionally, the process for producing the hydroxy sulfide-containing ester can form any hydroxy sulfide-containing ester as described herein.

DETD In some aspects, the reaction between the \*\*\*mercaptan\*\*\* and the unsaturated ester occurs in the presence of a solvent. In other aspects the reaction between the \*\*\*mercaptan\*\*\* and the unsaturated ester occurs in the substantial absence of a solvent. When the reaction occurs in the presence of a solvent, the solvent is selected from an aliphatic hydrocarbon, an ether, an aromatic compound, or any combination thereof. Generally, the solvent, regardless of its chemical class, can comprise

from 1 to 20 carbon atoms; alternatively, from 3 to 10 carbon atoms.  
When the solvent includes an aliphatic hydrocarbon, the aliphatic hydrocarbon is butane, isobutane, pentane, hexane, heptane, octane, or any mixture thereof. When the solvent includes an aromatic compound, the aromatic compound is benzene, toluene, xylene, ethylbenzene, or any mixture thereof. When the solvent includes an ether, the ether is diethyl ether, dipropyl ether, tetrahydrofuran, or any mixture thereof.

DETD When a solvent is used for the reaction between the \*\*\*mercaptan\*\*\* and the epoxidized unsaturated ester, the quantity of solvent can be any amount that facilitates the reaction, as understood by those of skill in the art. In some embodiments, the mass of the solvent is less than 30 times the mass of the epoxidized unsaturated ester. In other embodiments, the mass of the solvent is less than 20 times the mass of the epoxidized unsaturated ester; alternatively, less than 15 times the mass of the epoxidized unsaturated ester; alternatively, less than 10 times the mass of the epoxidized unsaturated ester; or alternatively, less than 5 times the mass of the epoxidized unsaturated ester. In other embodiments, the mass of the solvent is from 2 times to 20 times the mass of the epoxidized unsaturated ester; alternatively, from 3 times to 15 times the mass of the epoxidized unsaturated ester; alternatively, from 4 times to 15 times the mass of the epoxidized unsaturated ester; or alternatively, from 5 times to 10 times the mass of the epoxidized unsaturated ester.

DETD The reaction of the \*\*\*mercaptan\*\*\* and the epoxidized unsaturated ester can occur using any \*\*\*mercaptan\*\*\* to molar equivalents of \*\*\*epoxide\*\*\* groups in the epoxidized unsaturated ester (hereinafter referred to as " \*\*\*mercaptan\*\*\* to \*\*\*epoxide\*\*\* group molar ratio") that is capable of producing the herein described .alpha.-hydroxy \*\*\*thiol\*\*\* esters. The molar equivalents of epoxidized unsaturated ester epoxidized groups can be calculated by the equation: ##EQU4##

DETD In this equation, EUES GMW is the average gram molecular weight of the epoxidized unsaturated ester, EUES Mass is the mass of the epoxidized unsaturated ester, and EUES \*\*\*Epoxide\*\*\* is the average

number of  
     \*\*\*epoxide\*\*\* groups per epoxidized unsaturated ester  
molecule. In  
     some embodiments, the \*\*\*mercaptan\*\*\* to \*\*\*epoxide\*\*\*  
group  
     molar ratio is greater than 0.2. In other embodiments, the  
     \*\*\*mercaptan\*\*\* to \*\*\*epoxide\*\*\* group molar ratio is  
greater than  
     0.5; alternatively, greater than 1; or alternatively, greater  
than 2. In  
     other embodiments, the hydrogen sulfide to \*\*\*epoxide\*\*\*  
group molar  
     ratio ranges from 0.2 to 10; alternatively, from 0.5 to 8;  
     alternatively, from 0.75 to 5; or alternatively, from 1 to 3.

DETD In some aspects, the reaction of the \*\*\*mercaptan\*\*\* and the  
epoxidized unsaturated ester occurs in the presence of a  
catalyst.  
     Generally, the catalyst is any catalyst that is capable of  
catalyzing  
     the reaction of the \*\*\*mercaptan\*\*\* and the epoxidized  
unsaturated  
     ester to produce the desired hydroxy \*\*\*thiol\*\*\* ester. In  
one  
     aspect, the catalyst is selected from the group consisting of  
homogeneous and heterogeneous catalysts. In other aspects, the  
catalyst  
     is selected from the group consisting of zeolites, heterogeneous  
catalysts, homogeneous catalysts, and mixtures thereof. In  
another  
     aspect, the catalyst is an amine. In other aspects, the catalyst  
is  
     selected from the group consisting of cyclic conjugated amines,  
1,8-diazabicyclo[5.4.0]undec-7-ene, 1,5-diazabicyclo[4.3.0]non-5-  
ene,  
     and mixtures thereof.

DETD In some aspects, the reaction of the \*\*\*mercaptan\*\*\* and the  
epoxidized unsaturated ester occurs in the presence of a  
catalyst.  
     Generally, the catalyst is any catalyst that is capable of  
catalyzing  
     the reaction of the \*\*\*mercaptan\*\*\* and the epoxidized  
unsaturated  
     ester to produce the desired hydroxy \*\*\*thiol\*\*\* ester. In  
some  
     embodiments the catalyst is an organic base. In some embodiments,  
the  
     catalyst can be 1,8-diazabicyclo[5.4.0]undec-7-ene. (What other  
catalysts may be used?)

DETD The reaction of the \*\*\*mercaptan\*\*\* and the epoxidized  
unsaturated  
     ester can occur in a batch reactor or a continuous reactor. Any  
of the  
     batch or continuous reactors described herein can be used in this  
reaction. Other suitable reactors will be apparent to those of  
skill in  
     the art and are to be considered within the scope of the present  
invention.

DETD The time required for the reaction of the \*\*\*mercaptan\*\*\*  
and the  
     epoxidized unsaturated ester can be any reaction time required to

form

the described hydroxy sulfide-containing ester. Generally, the reaction

time is at least 15 minutes. In some embodiments, the reaction time

ranges from 15 minutes to 72 hours; alternatively, from 30 minutes to 48

hours; or alternatively, from 45 minutes to 36 hours.

DETD In some embodiments, the process to produce the hydroxy sulfide-containing ester further comprises a step to remove the residual

\*\*\*mercaptan\*\*\* after reacting the \*\*\*mercaptan\*\*\* and the

epoxidized unsaturated ester. In some embodiments the hydroxy sulfide-containing ester is vacuum stripped. In some embodiments,

the hydroxy sulfide-containing ester is vacuum stripped at a temperature

between 25.degree. C. and 250.degree. C.; or alternatively, between

50.degree. C. and 200.degree. C. In other embodiments, the hydroxy

sulfide-containing ester is sparged with an inert gas to remove the

\*\*\*mercaptan\*\*\*. In some embodiments, the hydroxy sulfide-containing

ester is sparged with an inert gas at a temperature between 25.degree.

C. and 250.degree. C.; or alternatively, between 50.degree. C. and

200.degree. C. In some aspects, the inert gas is nitrogen.

Generally,

the stripped or sparged hydroxy sulfide-containing ester comprises less

than 5 weight percent of the \*\*\*mercaptan\*\*\*. In other embodiments,

the stripped or sparged hydroxy sulfide-containing ester comprises less

than 2 weight percent of the \*\*\*mercaptan\*\*\*; alternatively, less

than 1 weight percent of the \*\*\*mercaptan\*\*\*; or alternatively, less

than 0.5 weight percent of the \*\*\*mercaptan\*\*\*.

DETD The reaction between the \*\*\*mercaptan\*\*\* and the epoxidized unsaturated ester can be performed at any reaction temperature

capable of forming the hydroxy sulfide-containing ester. In some embodiments,

the reaction temperature is greater than -20.degree. C. In other embodiments, the reaction temperature is greater than 0.degree.

C.;

alternatively, greater than 20.degree. C.; alternatively, greater than

50.degree. C.; or alternatively, greater than 80.degree. C. In yet other

embodiments, the reaction temperature ranges from -20.degree. C. to

200.degree. C.; alternatively, from 20.degree. C. to 170.degree. C.; or

alternatively, from 80.degree. C. to 140.degree. C.



DETD The reaction between the \*\*\*mercaptan\*\*\* and the epoxidized unsaturated ester can be performed at any reaction pressure that maintains the \*\*\*mercaptan\*\*\* and the epoxidized unsaturated ester in a substantially liquid state. In some embodiments, the reaction pressure ranges from 0 psig to 2000 psig. In other embodiments, the reaction pressure ranges from 0 psig to 1000 psig; alternatively, from 0 psig to 500 psig; or alternatively, from 0 psig to 200 psig.

DETD In another aspect, the process to produce a hydroxy sulfide-containing ester produces a hydroxy sulfide-containing ester having an \*\*\*epoxide\*\*\* group to sulfide group molar ratio less than 2.

Other hydroxy sulfide-containing ester \*\*\*epoxide\*\*\* group to sulfide group molar ratios are described herein. (The next passage needs to be incorporated into the hydroxy \*\*\*thiol\*\*\* ester section along with the first sentence of this paragraph.) Alternatively, the hydroxy sulfide-containing ester \*\*\*epoxide\*\*\* group to \*\*\*thiol\*\*\* group molar ratio can be less than 1.5; alternatively, less than 1.0;

alternatively, less than 0.5, alternatively, less than 0.25; or alternatively, less than 0.1. In other embodiments, the hydroxy sulfide-containing ester can be substantially free of \*\*\*epoxide\*\*\* groups.

DETD As an embodiment of the present invention, processes for producing a sulfonic acid-containing ester and for producing a sulfonate-containing ester are advantageously provided. Generally, the process for producing the sulfonic acid-containing ester comprises the steps of contacting a \*\*\*thiol\*\*\* ester and an oxidizing agent and oxidizing at least one \*\*\*thiol\*\*\* group of the \*\*\*thiol\*\*\* ester to produce a sulfonic acid group. The process for producing the sulfonate-containing ester comprises the steps of contacting a sulfonic acid-containing ester with a base and forming a sulfonate-containing ester.

DETD In an embodiment, the process to prepare a sulfonic acid-containing ester comprises the steps of contacting the \*\*\*thiol\*\*\* ester and the oxidizing agent and oxidizing the \*\*\*thiol\*\*\* ester to produce the sulfonic acid-containing ester. Generally the oxidizing agent oxidizes at least one \*\*\*thiol\*\*\* group of the \*\*\*thiol\*\*\* ester to a sulfonate group. The process to produce the sulfonic acid-containing ester composition can be applied to any \*\*\*thiol\*\*\*

ester described herein to prepare any sulfonic acid-containing ester described herein. In some embodiments, the \*\*\*thiol\*\*\* ester includes a hydroxy group. For example, the \*\*\*thiol\*\*\* ester can be any hydroxy \*\*\*thiol\*\*\* ester described herein. The oxidizing agent can be any oxidizing agent described herein.

DETD In some aspects, the oxidation of the \*\*\*thiol\*\*\* ester occurs in the presence of a solvent. In some aspects, the solvent is water.

DETD The oxidizing agent that is contacted with the \*\*\*thiol\*\*\* ester can be any oxidizing agent capable of oxidizing a \*\*\*thiol\*\*\* group to a sulfonic acid group. In some embodiments, the oxidizing agent is oxygen. In other embodiments, the oxidizing agent is chlorine. In other embodiments, the oxidizing agent is dimethyl sulfoxide. In yet other embodiments, the oxidizing agent is a combination of a hydrogen halide and a catalytic amount of a dialkyl sulfide, such as dimethyl sulfoxide.

Other suitable oxidizing agents will be apparent to those of skill in the art and are to be considered within the scope of the present invention.

DETD The oxidation of the \*\*\*thiol\*\*\* ester can be performed at any temperature capable of converting the \*\*\*thiol\*\*\* ester to a sulfonic acid-containing ester. In some embodiments, the \*\*\*thiol\*\*\* ester is oxidized at a temperature greater than -20.degree. C. In other embodiments, the \*\*\*thiol\*\*\* ester is oxidized at a temperature greater than 0.degree. C.; alternatively, greater than 20.degree. C.; or alternatively, greater than 50.degree. C.

DETD The time required for the oxidation of the \*\*\*thiol\*\*\* ester can be any time required to form the desired sulfonic acid-containing ester. Generally, the time required for the oxidation of the \*\*\*thiol\*\*\* ester is at least 15 minutes; alternatively, at least 30 minutes; alternatively, at least 45 minutes; or alternatively, at least 1 hour.

In some embodiments, the time required for the oxidation of the \*\*\*thiol\*\*\* ester ranges from 15 minutes to 12 hours; alternatively, from 30 minutes to 6 hours; alternatively, from 45 minutes to 3 hours.

DETD The oxidation of the \*\*\*thiol\*\*\* ester can be performed at any pressure that maintains the \*\*\*thiol\*\*\* ester and the oxidation agent in the proper state, which is not always a liquid state, to

oxidize the \*\*\*thiol\*\*\* ester to a sulfonic acid-containing ester. For example, when the oxidation agent is chlorine, the chlorine can be in the gaseous state. In some embodiments, the oxidation of the \*\*\*thiol\*\*\* ester can be performed at a pressure ranging from 0 to 2000 psig. In other embodiments, the oxidation of the \*\*\*thiol\*\*\* ester can be performed at a pressure ranging from 0 to 1000 psig; or alternatively, 0 to 500 psig.

DETD The oxidation of the \*\*\*thiol\*\*\* ester can be performed in a batch reactor or a continuous reactor, as described herein. Additionally, the process to produce the sulfonic acid-containing ester can comprise additional process steps as recognized by those skilled in the art.

DETD The formation of the sulfonate-containing ester can be performed at any temperature capable of converting the sulfonic acid group of the sulfonic acid-containing ester to a sulfonate group. In some embodiments, the sulfonate-containing ester is formed at a temperature greater than -20.degree. C. In other embodiments, the \*\*\*thiol\*\*\* ester is oxidized at a temperature greater than 0.degree. C.; alternatively, greater than 20.degree. C.; or alternatively, greater than 50.degree. C. In yet other embodiments, the \*\*\*thiol\*\*\* ester is oxidized at a temperature ranging from 0.degree. C. to 250.degree. C.; alternatively, from 0.degree. C. to 150.degree. C.; or alternatively, from 20.degree. C. to 100.degree. C.

DETD A preferred sulfur-containing vegetable oil is MVO available from Chevron Phillips Chemical Co. under the tradename Polymercaptan 358. Polymercaptan 358 is made by the free radical addition of hydrogen sulfide to the double bonds in soybean oil. Typically, Polymercaptan 358 has a \*\*\*thiol\*\*\* sulfur content of 5 to 10% and equivalent weights of 640 to 320, respectively.

DETD Another preferred sulfur-containing vegetable oil useful as part of the isocyanate-reactive component is a MHVO such as mercapto-hydroxy soybean oil. As described herein, a preferred mercapto-hydroxy soybean oil is made by the free radical addition of hydrogen sulfide to epoxidized soybean oil. Typically, the mercapto and hydroxy functionalities are equal and the \*\*\*mercaptan\*\*\* content is about 8.3% \*\*\*thiol\*\*\* sulfur. The equivalent weight of this material is 192, which

includes both mercapto and hydroxy functionalities.

DETD Yet another preferred sulfur-containing vegetable oil useful as part of the isocyanate-reactive component is a CMVO such as sulfur cross-linked mercaptanized soybean oil. Sulfur cross-linked mercaptanized soybean oil is made by the addition of elemental sulfur to mercaptanized soybean oil. In this process, a portion of the \*\*\*mercaptan\*\*\* groups are consumed as cross-linking sites for the sulfur. Typical sulfur cross-linked mercaptanized soybean oil products by Chevron Phillips Chemical Co. include Runs #22, 194, 195, 196 and 197 and have a \*\*\*thiol\*\*\* sulfur content ranging from about 8.0% to 1.4% and equivalent weights ranging from about 400 to about 2250, respectively.

DETD For epoxy polymer encapsulated CRF material made from sulfur-containing vegetable oil, it has been found that the use of a tertiary amine catalyst is highly preferred. The amount used is such to be sufficient to give the desired reaction rate for the production of the encapsulated slow release fertilizer product. A non-limiting example of a suitable amine catalyst is diazobicycloundecacene also known as 1,8-diazabicyclo[5,4,0]undec-7-ene [CAS# \*\*\*6674-22-2\*\*\* ] or "DBU", which is preferably used in the range of about 0.1% to 0.5% by weight of the coating. Other suitable catalyst materials will be apparent to those of ordinary skill in the art.

DETD The preferred sulfur-containing vegetable oil to be used in production of an epoxy polymer coated CRF material is MHVO such as mercapto-hydroxy soybean oil. One such material is mercapto-hydroxy soybean oil known as MHSO 566-84 produced by Chevron Phillips Chemical Co. This preferred material contains 8.33% \*\*\*thiol\*\*\* sulfur, with an equivalent weight of 384, based upon the \*\*\*mercaptan\*\*\* functionality.

DETD The unsaturated ester used as a feedstock to produce the \*\*\*thiol\*\*\* ester compositions described herein can be described using a number of different methods. One method of describing the unsaturated ester feedstock is by the number of ester groups and the number of carbon-carbon double bonds that comprise each unsaturated ester oil molecule. Suitable unsaturated ester used as a feedstock to produce the \*\*\*thiol\*\*\* ester compositions described herein minimally comprise at

least 1 ester group and at least 1 carbon-carbon double bond. However, beyond this requirement, the number of ester groups and carbon-carbon double bonds comprising the unsaturated esters are independent elements and can be varied independently of each other. Thus, the unsaturated esters can have any combination of the number of ester groups and the number of carbon-carbon double bonds described separately herein. Suitable, unsaturated esters can also contain additional functional groups such as alcohol, aldehyde, ketone, epoxy, ether, aromatic groups, and combinations thereof. As an example, the unsaturated esters can also comprise hydroxy groups. An example of an unsaturated ester that contains hydroxy groups is castor oil. Other suitable unsaturated esters will be apparent to those of skill in the art and are to be considered within the scope of the present invention.

DETD In yet another aspect, the polyol or mixture of polyols used to produce the unsaturated \*\*\*thiol\*\*\* ester has a molecular weight or average molecular weight less than 500. In other embodiments, the polyol or mixture of polyols have a molecular weight or average molecular weight less than 300; alternatively less than 200; alternatively, less than 150; or alternatively, less than 100.

DETD Specific carboxylic acids used as a component of the carboxylic acid composition used to produce the unsaturated ester oil can have from 3 to 30 carbon atoms per carboxylic acid molecule. In some embodiments the carboxylic acid is linear. In some embodiments the carboxylic acid is branched. In some embodiments the carboxylic acid is a mixture of linear and branched carboxylic acids. In some embodiments the carboxylic acid can also comprise additional functional groups including alcohols, aldehydes, ketones, and \*\*\*epoxides\*\*\*, among others.

DETD Minimally, the epoxidized unsaturated ester comprises at least one \*\*\*epoxide\*\*\* group. In an embodiment the epoxidized unsaturated ester comprises at least 2 \*\*\*epoxide\*\*\* groups; alternatively, at least 3 \*\*\*epoxide\*\*\* groups; or alternatively, at least 4 \*\*\*epoxide\*\*\*.

In other embodiments, the epoxidized unsaturated ester comprises from 2 to 9 \*\*\*epoxide\*\*\* groups; alternatively, from 2 to 4

\*\*\*epoxide\*\*\* groups; alternatively, from 3 to 8  
 \*\*\*epoxide\*\*\* groups; or alternatively, from 4 to 8 \*\*\*epoxide\*\*\* groups.  
 DETD In some embodiments, the unsaturated ester comprises a mixture  
 of epoxidized unsaturated esters. In this aspect, the number of  
 \*\*\*epoxide\*\*\* groups in the epoxidized unsaturated ester is  
 best described as an average number of \*\*\*epoxide\*\*\* groups per  
 epoxidized unsaturated ester molecule. In some embodiments, the  
 epoxidized unsaturated esters have an average of at least 1.5  
 \*\*\*epoxide\*\*\* groups per epoxidized unsaturated ester  
 molecule;  
 alternatively, an average of at least 2 \*\*\*epoxide\*\*\* groups  
 per epoxidized unsaturated ester molecule; alternatively, an average  
 of at least 2.5 \*\*\*epoxide\*\*\* groups per epoxidized unsaturated  
 ester molecule; or alternatively, an average of at least 3  
 \*\*\*epoxide\*\*\* groups per epoxidized unsaturated ester molecule. In other  
 embodiments,  
 the epoxidized unsaturated esters have average of from 1.5 to 9  
 \*\*\*epoxide\*\*\* groups per epoxidized unsaturated ester  
 molecule;  
 alternatively, an average of from 3 to 8 \*\*\*epoxide\*\*\* groups  
 per epoxidized unsaturated ester molecule; alternatively, an average  
 of from 2 to 4 \*\*\*epoxide\*\*\* groups per epoxidized unsaturated ester  
 molecule; or alternatively, from of 4 to 8 \*\*\*epoxide\*\*\*  
 group per epoxidized unsaturated ester molecule.  
 DETD The \*\*\*thiol\*\*\* composition can include an average of  
 greater than 0 to about 4 \*\*\*epoxide\*\*\* groups per triglyceride. The  
 \*\*\*thiol\*\*\* composition can also include an average of  
 greater than 1.5 to about 9 \*\*\*epoxide\*\*\* groups per triglyceride.  
 DETD \*\*\*Mercaptans\*\*\*  
 DETD Within some embodiments, an unsaturated ester or an epoxidized  
 unsaturated ester is contacted with \*\*\*mercaptan\*\*\*. Within  
 these embodiments, the \*\*\*mercaptan\*\*\* can be any \*\*\*mercaptan\*\*\*  
 comprising from 1 to 20 carbon atoms. Generally, the  
 \*\*\*mercaptan\*\*\*  
 can have the following structure:  $\text{HS}-\text{R}_{\text{sup.3}}$  wherein R<sub>3</sub> is  
 a C<sub>1</sub> to C<sub>20</sub> organyl groups or a C<sub>1</sub> to C<sub>20</sub> hydrocarbyl groups. In further  
 embodiments the R<sub>3</sub> can be a C<sub>2</sub> to C<sub>10</sub> organyl group or a C<sub>2</sub> to  
 C<sub>10</sub> hydrocarbyl group. In some embodiments, the \*\*\*mercaptan\*\*\*  
 composition comprises a solvent. In one aspect, the  
 \*\*\*mercaptan\*\*\*  
 composition comprises at least one other functional group.  
 DETD The at least one other functional group can be selected from  
 several different groups. For example, the at least one other functional  
 group

is an alcohol group, a carboxylic alcohol group, a carboxylic ester group, an amine group, a sulfide group, a \*\*\*thiol\*\*\* group, a methyl or ethyl ester of a carboxylic acid group, or combinations thereof. Other types of functional groups will be apparent to those of skill in the art and are to be considered within the scope of the present invention.

DETD In some embodiments, the \*\*\*mercaptan\*\*\* is selected from the group consisting of 3-mercaptopropyl-trimethoxysilane, 2-mercaptopyridine, 4-mercaptopyridine, 2-mercaptopyrimidine, mercaptopyruvic acid, mercaptosuccinic acid, 2-mercaptonicotinic acid, 6-mercaptonicotinic acid, 2-mercaptophenol, 4-mercaptophenol, 3-mercapto-1,2-propanediol, 3-mercapto-1,2-propanediol, 3-mercapto-1-propanesulfonic acid, 1-mercapto-2-propanol, 3-mercapto-1-propanol, 2-mercaptopropionic acid, 3-mercaptopropionic acid, 2-mercaptobenzyl alcohol, 3-mercapto-2-butanol, 4-mercapto-1-butanol, 2-mercaptoethanesulfonic acid, 2-mercaptoethanol, 2-mercaptoethyl ether, 2-mercaptoethyl sulfide, 16-mercaptohexadecanoic acid, 6-mercapto-1-hexanol, 4'-mercaptoacetanilide, mercaptoacetic acid, 2-mercaptobenzoic acid, 3-mercaptobenzoic acid, 4-mercaptobenzoic acid, 2-mercaptothiazoline, 3-mercapto-1H-1,2,4-triazole, 11-mercaptoundecanoic acid, 1-mercapto-1-undecanol, or combinations thereof.

DETD In some embodiments, the \*\*\*mercaptan\*\*\* is selected from the group consisting of beta-mercaptoethanol, 2-mercaptophenol, 3-mercaptophenol, 4-mercaptophenol, 1-mercapto-2-propanol, 1-mercapto-3-propanol, mercaptoacetic acid, 2-mercaptopropionic acid, 3-mercaptopropionic acid, 2-mercaptobenzoic acid, 3-mercaptobenzoic acid, 4-mercaptobenzoic acid, 2-mercaptobenzylalcohol, 3-mercapto-2-butanol, 4-mercapto-1-butanol, 2-mercaptoethyl ether, 2-mercaptoethyl sulfide, 6-mercapto-hexanol, 3-mercapto-1,2-propanediol, mercaptosuccinic acid, and mixtures thereof.

In further embodiments, the \*\*\*mercaptan\*\*\* is selected from the group consisting of beta-mercaptoethanol, 1-mercapto-2-propanol, 1-mercapto-3-propanol, 2-mercaptobenzylalcohol, 3-mercapto-2-butanol, 4-mercapto-1-butanol, 6-mercapto-hexanol, 3-mercapto-1,2-propanediol, and mixtures thereof. In further embodiments, the \*\*\*mercaptan\*\*\* is selected from the group consisting 2-mercaptophenol, 3-mercaptophenol, 4-mercaptophenol, and mixtures thereof. In yet further

embodiments, the  
\*\*\*mercaptan\*\*\* is selected from the group consisting  
mercaptoacetic  
acid, 2-mercaptopropionic acid, 3-mercaptopropionic acid,  
2-mercaptobenzoic acid, 3-mercaptobenzoic acid, 4-mercaptobenzoic  
acid,  
mercaptosuccinic acid, and mixtures thereof.  
DETD Within some embodiments, the inventive compositions described  
herein  
are reacted with an isocyanate compound to produce a  
polythiourethane  
composition. The isocyanate may be any isocyanates capable of  
reacting  
with the \*\*\*thiol\*\*\* esters, hydroxy \*\*\*thiol\*\*\* esters,  
and a  
cross-linked \*\*\*thiol\*\*\* esters described herein to form a  
polyurethane composition. Generally, the isocyanate compound has  
at  
least two isocyanate groups.  
DETD In order to quantitatively measure the \*\*\*thiol\*\*\* sulfur,  
the  
\*\*\*thiol\*\*\* sulfur analyses were conducted using silver  
nitrate  
titration in accordance with ASTM D3227, with the following  
modifications designed to minimize probe fouling by silver salts:  
the  
samples were diluted in a known mass of tetrahydrofuran. The  
silver  
nitrate concentration was 0.01 N standardized against potassium  
iodide.  
DETD \*\*\*Thiol\*\*\* sulfur was analyzed by three different tests.  
The first  
test used was the modified ASTM D3227, which resulted in a  
\*\*\*thiol\*\*\*  
sulfur measurement of 4.64%. The second test used to measure the  
\*\*\*thiol\*\*\* sulfur was SLP-1204, which is a test developed by  
Chevron  
Phillips Chemical Company LLP. By using the SLP-1204 test, the  
resulting  
\*\*\*thiol\*\*\* sulfur measurement was 4.28%. Lastly, the total  
sulfur was  
measured by combustion analysis, which resulted in a total sulfur  
measurement of 4.27%.  
DETD Vegetable oil (42 kg) was charged to a 100-gallon holding  
vessel. The  
vessel was purged with nitrogen and returned to atmospheric  
pressure.  
Hydrogen sulfide (174 kg) was charged to the holding vessel. The  
vessel  
temperature was controlled from 25-30.degree. C. while the  
pressure was  
typically maintained between 380-400 psig. The reactants were  
continuously rolled from the holding tank through a stainless  
steel  
tubular photochemical reactor containing a 7.5 KW Hanovia medium  
pressure mercury lamp contained within a quartz tube. Reactor  
temperature, pressure, and composition were monitored over the  
course of  
the reaction. The reaction time was dependent upon reaching a  
desired



composition of \*\*\*thiol\*\*\* sulfur. Upon completion, the unreacted hydrogen sulfide was slowly vented from the system. Residual H.sub.2S was removed at 100.degree. C. and reduced pressure while passing nitrogen through a nitrogen sparge tube. The product was drained from the bottom of the reactor into a clean drum. The \*\*\*thiol\*\*\* sulfur measurements were 11.0% when using the modified ASTM D3227, 8.74% when using SLP-1204, and the total sulfur was 11.21% when using combustion analysis (total sulfur).

DETD The resulting mercaptanized soybean oil was subjected to nitrogen sparging under reduced pressure at 100.degree. C. for a period of 4 hours to remove any residual hydrogen sulfide. The \*\*\*thiol\*\*\* sulfur measurements were 13.0% when using the modified ASTM D3227, 9.82% when using SLP-1204, and 11.69% when using combustion analysis.

DETD Table 1 provides the properties of the mercaptanized soybean oil produced in examples 1-3.

TABLE 1

#### Mercaptanized Soybean Oil Product Properties

Example	Cyclic Sulfide to ***Thiol*** Sulfur.sup..dagger. Group		
	to ***Thiol*** (wt %)	groups Molar Ratio	Molar Ratio
1	4.28	0.02	2.79
2	11.0	0.03	0.26
3	13.0	0.03	0.51

.sup..dagger. \*\*\*Thiol\*\*\* sulfur content determined by the modified ASTM

D3227

DETD Soybean oil was charged to a 1000 gallon stirred reactor. Hydrogen sulfide was then charged to the reactor. After the hydrogen sulfide was charged to the reactor, the stirrers and the UV lamps were turned on and the reaction allowed to build temperature and pressure as the reaction proceed. The reaction was continued until a minimum \*\*\*thiol\*\*\* sulfur content of 8 weight percent was achieved. After reaction was completion, the excess hydrogen sulfide was flashed from the reactor.

For runs 2-5, the mercaptanized soybean oil product underwent an additional hydrogen sulfide stripping step comprising stripping hydrogen sulfide from the product under vacuum, 50 mm Hg, at 250.degree. F. (only true for runs 2-5).

DETD Table 3 provides the details of the analysis of the mercaptanized soybean oil producing in the five 1000 gallon reactor runs.

TABLE 3  
1000 gallon reactor Mercaptanized Soybean Oil Product Properties

Run Number	***Thiol***		Cyclic Sulfide to		***Thiol*** Side Chain	
	Sulfur.sup..dagger. Group		Molar Ratio		C.dbd.C groups	
	(wt %)	Molar Ratio				(%)
1	9.3	--	--			71.6
2	9.6	0.04	0.48			72.3
3	9.2	0.03	0.59			69.1
4	9.3	0.03	0.62			71.6
5	10.1	0.03	0.54			72.3

.sup..dagger. \*\*\*Thiol\*\*\* sulfur content determined by Raman spectroscopy  
Mercaptanized Castor Bean Oil  
DETD The analytical properties of the two mercaptanized castor oil products are provide in Table 4.

TABLE 4  
Mercaptanized Castor Oil Product Properties

Containing	***Thiol***		C.dbd.C to		Side Chain	
	Sulfur.sup..dagger. Group		Molar Ratio		groups	
***Thiol***	(wt %)					(%)
Example						
1	6.4	0.52	64.1			
2	7.4	0.26	77.7			

.sup..dagger. \*\*\*Thiol\*\*\* sulfur content determined by Raman spectroscopy  
Mercaptohydroxy Soybean Oil Synthetic Procedure  
DETD Epoxidized Soybean Oil (700 g, .about.0.7 mol) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 4.7 g, 30.5 mmol) were charged to a 1-L Hastelloy C autoclave reactor that was pressure tested to 630 psig. Hydrogen sulfide (H.sub.2S, 132.0 g, 3.87 mol) was then pressured into the stirred reactor contents through a dip tube in the liquid space. The reaction mixture was heated and maintained at 85.degree. C. with stirring for 8 hrs, during which time the reactor pressure decreased from a maximum of 351 psig to 219 psig. The stirrer was stopped and while still warm (80-85.degree. C.), excess H.sub.2S was slowly vented to a low-pressure flare. The reactor vapor space

was then swept with N.sub.2 for 1 hr and the reactor contents drained warm (80-85.degree. C.). The reaction product was N.sub.2 sparged under vacuum (<5 mmHg) at 130-140.degree. C. for 16 hrs to remove residual H.sub.2S. The resulting light yellow, viscous sticky oil had a \*\*\*thiol\*\*\* sulfur (titration by modified ASTM D3227) content of 7.53 wt. %, 2.5 SH/molecule, or 2.35 meq SH/g. Combustion analysis indicated C, 64.37%, H, 10.20%, N, <0.15%, and S, 9.51%.

DETD Epoxidized Soybean Oil (600 g, .about.0.6 mol) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 5.0 g, 32.4 mmol) were charged to a 1-L Hastelloy C autoclave reactor, and the vessel was pressure tested to 630 psig. Hydrogen sulfide (H.sub.2S, 204.0 g, 5.99 mol) was then pressured into the stirred reactor contents through a dip tube in the liquid space. The reaction mixture was heated and maintained at 97.degree. C. with stirring for 14 hrs, during which time the reactor pressure decreased from a maximum of 509 psig to 229 psig. The stirrer was stopped and while still warm (90-95.degree. C.), excess H.sub.2S was slowly vented to a low-pressure flare. The reactor vapor space was then swept with N.sub.2 for 1 hr and the reactor contents drained warm (80-85.degree. C.). The reaction product was N.sub.2 sparged under vacuum (<50 mmHg) at 130-140.degree. C. for 16 hrs to remove residual H.sub.2S. The resulting light yellow, viscous sticky oil had a \*\*\*thiol\*\*\* sulfur (titration by modified ASTM D3227) content of 4.14 wt. %, 1.4 SH/molecule, or 1.29 meq SH/g. Combustion analysis indicated C, 65.18%, H, 10.17%, N, <0.15%, and S, 7.80%.

DETD Epoxidized Soybean Oil (600 g, .about.0.6 mol) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 5.0 g, 32.4 mmol) were charged to a 1-L Hastelloy C autoclave reactor, and the vessel was pressure tested to 630 psig. Hydrogen sulfide (H.sub.2S, 204.0 g, 5.99 mol) was then pressured into the stirred reactor contents through a dip tube in the liquid space. The reaction mixture was heated and maintained at 85.degree. C. with stirring for 10 hrs, during which time the reactor pressure decreased from a maximum of 578 psig to 489 psig. The stirrer was stopped and while still warm (80-85.degree. C.), excess H.sub.2S was slowly vented to a low-pressure flare. The reactor vapor space

was then swept with N.sub.2 for 1 hr and the reactor contents drained warm (80-85.degree. C.). The reaction product was N.sub.2 sparged under vacuum (<50 mmHg) at 130-140.degree. C. for 16 hrs to remove residual H.sub.2S. The resulting light yellow, viscous sticky oil had a \*\*\*\*thiol\*\*\* sulfur (titration with modified ASTM D3227) content of 8.28 wt. %, 2.8 SH/molecule, or 2.58 meq SH/g. Combustion analysis indicated C, 65.24%, H, 9.52%, N, 0.18%, and S, 9.53%.

DETD Epoxidized soybean oil (600 g, .about.0.6 mol) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 5.0 g, 32.4 mmol) were charged to a 1-L Hastelloy C autoclave reactor that was pressure tested to 630 psig. Hydrogen sulfide (H.sub.2S, 204.0 g, 5.99 mol) was then pressured into the stirred reactor contents through a dip tube in the liquid space. The reaction mixture was heated and maintained at 85.degree. C. with stirring for 12 hrs, during which time the reactor pressure decreased from a maximum of 587 psig to 498 psig. The stirrer was stopped and while still warm (80-85.degree. C.), excess H.sub.2S was slowly vented to a low-pressure flare. The reactor vapor space was then swept with N.sub.2 for 1 hr and the reactor contents drained warm (80-85.degree. C.). The reaction product was N.sub.2 sparged under vacuum (<50 mmHg) at 130-140.degree. C. for 16 hrs to remove residual H.sub.2S. The resulting light yellow, viscous sticky oil had a \*\*\*\*thiol\*\*\* sulfur (titration by modified ASTM D3227) content of 8.24 wt. %, 2.8 SH/molecule, or 2.57 meq SH/g. Combustion analysis indicated C, 63.39%, H, 10.01%, N, <0.15%, and S, 8.76%.

DETD Epoxidized soybean oil (600 g, .about.0.6 mol) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 5.0 g, 32.4 mmol) were charged to a 1-L Hastelloy C autoclave reactor, and the vessel was pressure tested to 630 psig. Hydrogen sulfide (H.sub.2S, 204.0 g, 5.99 mol) was then pressured into the stirred reactor contents through a dip tube in the liquid space. The reaction mixture was heated and maintained at 85.degree. C. with stirring for 8 hrs, during which time the reactor pressure decreased from a maximum of 606 psig to 537 psig. The stirrer was stopped and while still warm (80-85.degree. C.), excess H.sub.2S was slowly vented to a low-pressure flare. The reactor vapor space was then swept with N.sub.2 for 1 hr and the reactor contents drained warm

(80–85.degree. C.). The reaction product was N.sub.2 sparged under vacuum (<50 mmHg) at 130–140.degree. C. for 16 hrs to remove residual H.sub.2S. The resulting light yellow, viscous sticky oil had a \*\*\*thiol\*\*\* sulfur (titration by modified ASTM D3227) content of 7.34 wt. %, 2.5 SH/molecule, or 2.29 meq SH/g. Combustion analysis indicated C, 64.47%, H, 10.18%, N, <0.15%, and S, 8.40%.

DETD Epoxidized soybean oil (600 g, .about.0.6 mol) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 5.0 g, 32.4 mmol) were charged to a 1-L Hastelloy C autoclave reactor that was pressure tested to 630 psig. Hydrogen sulfide (H.sub.2S, 204.0 g, 5.99 mol) was then pressured into the stirred reactor contents through a dip tube in the liquid space. The reaction mixture was heated and maintained at 85.degree. C. with stirring for 6 hrs, during which time the reactor pressure decreased from a maximum of 586 psig to 556 psig. The stirrer was stopped and while still warm (80–85.degree. C.), excess H.sub.2S was slowly vented to a low-pressure flare. The reactor vapor space was then swept with N.sub.2 for 1 hr and the reactor contents drained warm (80–85.degree. C.). The reaction product was N.sub.2 sparged under vacuum (<50 mmHg) at 130–140.degree. C. for 16 hrs to remove residual H.sub.2S. The resulting light yellow, viscous sticky oil had a \*\*\*thiol\*\*\* sulfur (titration by modified ASTM D3227) content of 5.93 wt. %, 2.0 SH/molecule, or 1.85 meq SH/g. Combustion analysis indicated C, 65.26%, H, 10.19%, N, <0.15%, and S, 8.43%.

DETD Epoxidized soybean oil (600 g, .about.0.6 mol) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 5.0 g, 32.4 mmol) were charged to a 1-L Hastelloy C autoclave reactor, and the vessel was pressure tested to 630 psig. Hydrogen sulfide (H.sub.2S, 204.0 g, 5.99 mol) was then pressured into the stirred reactor contents through a dip tube in the liquid space. The reaction mixture was heated and maintained at 85.degree. C. with stirring for 4 hrs, during which time the reactor pressure decreased from a maximum of 595 psig to 554 psig. The stirrer was stopped and while still warm (80–85.degree. C.), excess H.sub.2S was slowly vented to a low-pressure flare. The reactor vapor space was then swept with N.sub.2 for 1 hr and the reactor contents drained warm (80–85.degree. C.). The reaction product was N.sub.2 sparged under

vacuum (<50 mmHg) at 130-140.degree. C. for 16 hrs to remove residual

H.sub.2S. The resulting light yellow, viscous sticky oil had a \*\*\*thiol\*\*\* sulfur (titration by modified ASTM D3227) content of 5.36 wt. %, 1.8 SH/molecule, or 1.67 meq SH/g. Combustion analysis indicated C, 65.67%, H, 10.17%, N, 0.34%, and S, 9.84%.

DETD Epoxidized soybean oil (600 g, .about.0.6 mol) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 5.0 g, 32.4 mmol) were charged to a 1-L Hastelloy C autoclave reactor that was pressure tested to 630 psig. Hydrogen sulfide (H.sub.2S, 204.0 g, 5.99 mol) was then pressured into the stirred reactor contents through a dip tube in the liquid space. The reaction mixture was heated and maintained at 85.degree. C. with stirring for 4 hrs, during which time the reactor pressure decreased from a maximum of 577 psig to 519 psig. The stirrer was stopped and while still warm (80-85.degree. C.), excess H.sub.2S was slowly vented to a low-pressure flare. The reactor vapor space was then swept with N.sub.2 for 1 hr and the reactor contents drained warm (80-85.degree. C.). The reaction product was N.sub.2 sparged under vacuum (<50 mmHg) at 130-140.degree. C. for 16 hrs to remove residual

H.sub.2S. The resulting light yellow, viscous sticky oil had a \*\*\*thiol\*\*\* sulfur (titration with AgNO.sub.3) content of 5.85 wt. %, 2.0 SH/molecule, or 1.82 meq SH/g. Combustion analysis indicated C, 65.09%, H, 10.15%, N, 0.35%, and S, 10.63%.

DETD Epoxidized soybean oil (600 g, .about.0.6 mol) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 5.0 g, 32.4 mmol) were charged to a 1-L Hastelloy C autoclave reactor, and the vessel was pressure tested to 630 psig. Hydrogen sulfide (H.sub.2S, 204.0 g, 5.99 mol) was then pressured into the stirred reactor contents through a dip tube in the liquid space. The reaction mixture was heated and maintained at 85.degree. C. with stirring for 2 hrs, during which time the reactor pressure decreased from a maximum of 577 psig to 508 psig. The stirrer was stopped and while still warm (80-85.degree. C.), excess H.sub.2S was slowly vented to a low-pressure flare. The reactor vapor space was then swept with N.sub.2 for 1 hr and the reactor contents drained warm (80-85.degree. C.). The reaction product was N.sub.2 sparged under vacuum (<5 mmHg) at 130-140.degree. C. for 16 hrs to remove residual

H.sub.2S. The resulting light yellow, viscous sticky oil had a  
 \*\*\*thiol\*\*\* sulfur (titration by modified ASTM D3227) content  
 of 5.07

wt. %, 1.7 SH/molecule, or 1.58 meq SH/g. Combustion analysis  
 indicated

C, 63.96%, H, 10.01%, N, 0.35%, and S, 11.22%.

DETD Table 5 provides the properties of the mercaptohydroxy soybean  
 oil

samples produced in Examples 1-10.

TABLE 5

per Example	***Epoxides***		***Mercaptan***		
	Reaction	Reaction	Sulfur	SH per	groups left
	Time (hrs) molecule.sup.3	Temp (.degree. C.) :SH Molar Ratio	(wt. %).sup.1	molecule.sup.2	
1	0	N/A	N/A	0	4.3
--					
2	8	85	7.53	2.5	1.8
	0.72				
3	14	97	4.14	1.4	2.9
	2.07				
4	10	85	8.28	2.8	1.5
	0.54				
5	12	85	8.24	2.8	1.5
	0.54				
6	8	85	7.34	2.5	1.8
	0.72				
7	6	85	5.93	2.0	2.3
	1.15				
8	4	85	5.36	1.8	2.5
	1.40				
9	4	85	5.85	2.0	2.3
	1.15				
10	2	85	5.07	1.7	2.6
	1.529				

.sup.1Thiol sulfur was determined by silver nitrate oxidation using ASTM  
 D 3227

.sup.2Determined by wt. % \*\*\*thiol\*\*\* sulfur

.sup.3Determined by subtracting the SH/molecule from the starting  
 material

\*\*\*epoxide\*\*\* content

DETD Epoxidized soybean oil and the catalyst were charged to a 1-L  
 Hastelloy

C autoclave reactor, and the vessel was pressure tested to 1000  
 psig.

Hydrogen sulfide was then pressured into the stirred reactor  
 contents

through a dip tube in the liquid space. The reaction mixture was  
 heated

and maintained at temperature a set period of time with stirring  
 for 12

hrs. During the reaction time the reactor pressure usually  
 decreased. At

the end of the reaction time, the stirrer was stopped and excess H.sub.2S was slowly vented while the reaction mixture was warm to a low-pressure flare. The reactor vapor space was then swept with N.sub.2 for 1 hr and the reactor contents drained. The reaction product was N.sub.2 sparged under vacuum (<50 mmHg) at 100.degree. C. for 16 hrs to remove residual H.sub.2S. Table 6 provides the reaction conditions used to produce the mercaptohydroxy soybean oils for several runs and the sulfur content of the mercaptohydroxy soybean oils produced.

TABLE 6

# Mercaptohydroxy Soybean Oil Production Runs

Run	Epoxidized Soybean Oil Temperature (g)	Catalyst Time (g)	H.sub.2S (g)	H.sub.2S: Sulfur.sup.a Molar Ratio	***Epoxide*** Sulfur (.degree. C.)
(minutes)	(wt. %)		***Thiol***		
556-41.sup..dagger.	249.6		1.950	214.0 5.86	64
728	5.69				
556-53.sup..dagger.	250.0		2.000	213.0 5.81	100
370	9.04				
556-47.sup..dagger.	250.5		1.050	213.0 5.81	101
720	10.47				
407-81D.sup..dagger.	500.0		4.200	255.0 3.49	85
480	7.53				
407-86.sup..dagger.	600.0		5.000	204.0 2.07	85
600	8.28				
556-79.sup..dagger-dbl.	250.0		2.600	214.0 5.83	100
720	6.68				
556-80.sup..dagger-dbl.	251.0		5.000	214.0 5.81	100
720	9.51				

.sup..dagger.Catalyst was DBU

.sup..dagger-dbl.catalyst was triethylamine (TEA)

.sup.aThiol sulfur measured by silver nitrate titration using modified ASTM D

3227

DETD Run number 407-86 was subjected to the sodium methoxide methanolysis

procedure and subsequently analyzed by GC/MS. The GS/MS analysis indicated that the product had \*\*\*epoxide\*\*\* group to

\*\*\*thiol\*\*\*

group molar ratio of approximately 0.14. The methanolysis data

also

indicated that an average of 80.4 percent of the product

mercaptohydroxy

soybean oil contained sulfur.

DETD Mercaptanized soybean oil (900.1 g; 10.92 wt. % sulfur,) was charged to a three necked flask along with elemental sulfur



pellets (9.6 g). The reaction mixture was heated to 120.degree.  
 C. until  
 sulfur dissolved and then cooled to 99.degree. C. Tributylamine  
 (4.8 g)  
 was charged to the reaction mixture with an addition funnel drop  
 wise.  
 The reaction mixture was mixed at 90.degree. C. for 2 hrs.  
 H.sub.2S  
 evolution was observed. The reaction product (904.8 g) was  
 sparged with  
 N.sub.2 under vacuum at 110.degree. C. for 4 hrs to remove  
 residual  
 H.sub.2S. The final product was a light yellow oil with a  
 \*\*\*thiol\*\*\*  
 sulfur of 6.33 wt. % (by modified ASTM D3227). The elemental  
 combustion  
 analysis was 70.19% C, 10.37% H; and 11.21% S.  
 DETD Mercaptanized soybean oil (900.0 g; 10.92 wt. % \*\*\*thiol\*\*\*  
 sulfur,) was charged to a three necked flask along with elemental  
 sulfur  
 pellets (36.0 g). The reaction mixture was heated to 120.degree.  
 C.  
 until sulfur dissolved and then cooled to 100.degree. C.  
 Tributylamine  
 (4.8 g) was charged to the reaction mixture with an addition  
 funnel drop  
 wise. The reaction mixture was mixed at 90.degree. C. for 36 hrs.  
 H.sub.2S evolution was observed. The reaction product (825.6 g)  
 was  
 sparged with N.sub.2 under vacuum at 90.degree. C. for 36 hrs to  
 remove  
 residual H.sub.2S. The reaction product was then sparged with  
 N.sub.2  
 under vacuum at 110.degree. C. for 3 hrs to remove residual  
 H.sub.2S.  
 The final product was a light yellow oil with a \*\*\*thiol\*\*\*  
 sulfur  
 of 2.36 wt. % (by modified ASTM D3227). The elemental combustion  
 analysis was 68.90% C; 11.07% H; and 12.25% S.  
 DETD Mercaptanized soybean oil (900.1 g; 10.92 wt. % \*\*\*thiol\*\*\*  
 sulfur,) was charged to a three necked flask along with elemental  
 sulfur  
 pellets (18.0 g). The reaction mixture was heated to 125.degree.  
 C.  
 until sulfur dissolved and then cooled to 101.degree. C.  
 Tributylamine  
 (4.8 g) was charged to the reaction mixture with an addition  
 funnel drop  
 wise. The reaction mixture was mixed at 90.degree. C. for 2 hrs.  
 H.sub.2S evolution was observed. The reaction product (901.5 g)  
 was  
 sparged with N.sub.2 under vacuum at 110.degree. C. for 4 hrs to  
 remove  
 residual H.sub.2S. The final product was a light yellow oil with  
 a  
 \*\*\*thiol\*\*\* sulfur of 4.9 wt. % (by modified ASTM D3227). The  
 elemental combustion analysis was 69.58% C, 11.25% H; and 11.31%  
 S.  
 DETD Mercaptanized soybean oil (900.2 g; 10.92 wt. % \*\*\*thiol\*\*\*  
 sulfur,) was charged to a three necked flask along with elemental

sulfur pellets (45.0 g). The reaction mixture was heated to 125.degree. C. until sulfur dissolved and then cooled to 100.degree. C. Tributylamine (4.8 g) was charged to the reaction mixture with an addition funnel drop wise. The reaction mixture was mixed at 90.degree. C. for 2 hrs. H.sub.2S evolution was observed. The reaction product (915.0 g) was sparged with N.sub.2 under vacuum at 110.degree. C. for 4 hrs to remove residual H.sub.2S. The final product was a light yellow oil with a \*\*\*thiol\*\*\* sulfur of 1.41 wt. % (by modified ASTM D3227). The elemental combustion analysis was 68.35% C, 10.98% H; and 13.28% S. Numerous polythiourethane compositions were prepared by reacting a \*\*\*thiol\*\*\* ester composition with a diisocyanate in the presence of a catalyst by using the processes described herein for preparing such polythiourethane compositions. The compositions were produced using the different variables of feedstocks, diisocyanates, stoichiometry, and catalysts shown in Table 8. Once every combination of variable was used, over 1200 compositions were produced. Each of the feedstocks were reacted with each of the diisocyanates at each of the stoichiometries with each of the catalysts listed to produce the 1200+ compositions. The stoichiometry was based upon a \*\*\*thiol\*\*\* ester composition (MSO, MHSO, CMSO, MCO) active hydrogen ( \*\*\*thiol\*\*\* and hydroxyl group) to diisocyanate equivalent ratio. For example, castor oil was reacted with toluene diisocyanate at a stoichiometric value of 1.25 while using Jeffol.RTM. A-480 as the catalyst. As another example, a \*\*\*thiol\*\*\* ester composition was reacted with methane diisocyanate at a stoichiometric value of 0.9 while using the DABCO catalyst. DETD In the first MCO polythiourethane example, MCO was weighed into a polyethylene beaker. To the MCO agent was added Luprinate at a \*\*\*thiol\*\*\* to isocyanate mole ratio of 0.95. To this reaction mixture was added dibutyl tin dilaurate (DBTDL) at a weight percent of 0.125 based upon the total weight of the ingredients. The three-component reaction mixture was then manually stirred with a wooden Popsicle stick. The entire pre-polymer mixture was then poured into a mold for curing

and cured using curing profile B. After the curing time was complete it was determined that the preparation produced a polythiourethane polymer.

DETD In the second MCO polythiourethane example, MCO was weighed into a polyethylene beaker. To the MCO agent was added Luprinate M20S at a \*\*\*thiol\*\*\* to isocyanate mole ratio of 1.00. To this reaction mixture was added dibutyl tin dilaurate (DBTDL) at a weight percent of 0.125 based upon the total weight of the ingredients. The three-component reaction mixture was then manually stirred with a wooden Popsicle stick. The entire pre-polymer mixture was then poured into a mold for curing and cured using curing profile B. After the curing time was complete it was determined that the preparation produced a polythiourethane polymer.

DETD In the polythiourethane compositions, the feedstock \*\*\*thiol\*\*\* ester compositions that were used included MSO (mercaptanized soybean oil), MHSO (mercaptohydroxy soybean oil), CMSO (cross-linked mercaptanized soybean oil), castor oil, and MCO (mercaptanized castor oil). The diisocyanates that were used to produce these compositions included MDI (4,4'-methylenebis(phenyl) diisocyanate), HMDI (4,4'-methylenebis(cyclohexyl) diisocyanate, which is also known as hydrogenated MDI), TDI (tolylene 2,4-diisocyanate), HDI (1,6-diisocyanatohexane, which is also known as hexamethylene diisocyanate), and Luprinate.TM. M20S (which is an oligomerized form of MDI and is also referred to as polymeric MDI that is produced by BASF Corporation). The catalysts that were used included DABCO (diazabicyclooctane--di-tertiary amine), DBTDL (dibutyl tin dilaurate--organometallic catalyst), Jeffol.RTM. A-480 (which is a tertiary amine polyol produced by Huntsman Based Chemicals), and BDMA (benzyl dimethylamine).

DETD In the Fertilizer Examples, the following materials were used:

A: Fertilizer particles--granular fertilizer grade urea, SGN 250, commercially available from Agrium;

B1: Mercaptanized soybean oil (an example of MVO discussed above)--Polymercaptan 358, available from Chevron Phillips Chemical Co.;

8.65% \*\*\*thiol\*\*\* sulfur; 370 equivalent weight; viscosity of 510.6 cSt @ 21.degree. C.;

B2: Mercapto-hydroxy soybean oil (an examples of MHVO discussed above)--A

mercapto-hydroxy soybean oil made by the free radical addition of hydrogen sulfide to epoxidized soybean oil; the mercapto and hydroxy functionalities are equal; 8.335% \*\*\*thiol\*\*\* sulfur; equivalent weight 192 (including both mercapto and hydroxy functionalities); B3: Sulfur cross-linked mercaptanized soybean oil (an example of CMVO discussed above)--A sulfur cross-linked mercaptanized soybean oil made by the addition of elemental sulfur to mercaptanized soybean oil; \*\*\*thiol\*\*\* sulfur content 6.33%; equivalent weight 506; B4: Sulfur cross-linked mercaptanized soybean oil (an example of CMVO discussed above)--A sulfur cross-linked mercaptanized soybean oil made by the addition of elemental sulfur to mercaptanized soybean oil; \*\*\*thiol\*\*\* sulfur content 7.64%; equivalent weight 419; cross-linkcross-link C1: Isocyanate #17--A polymeric MDI, commercially available from BASF Canada, equivalent weight of 133; C2: Epoxy resin--5 minute epoxy resin, commercially available from ITW Devcon, Danvers, Mass. 01923 USA, equivalent weight 198; D1: Organic additive--Gulftene C30-HA alpha olefin wax, commercially available from Chevron Phillips Chemical Co., melting point 65.degree. C.-80.degree. C.; D2: Organic additive--Calwax 170, a microcrystalline wax commercially available from Calwax Corporation; E: Cross-linking agent--Jeffol A480, commercially available from Huntsman Polyurethanes; equivalent weight of 120; functionality 4.0; viscosity of 4000 cPs @25C; F1: Amine catalyst: Exp-9, commercially available from Huntsman Polyurethanes; and F2: Amine catalyst: 1,8-Diazabicyclo[5,4,0]undec-7-ene (DBU), CAS# \*\*\*6674-22-2\*\*\* .

DETD Analysis of the \*\*\*Thiol\*\*\* Containing Esters, Hydroxy \*\*\*Thiol\*\*\* Containing Esters and Cross-Linked \*\*\*Thiol\*\*\* Containing Ester

DETD Particular aspects of the \*\*\*thiol\*\*\* containing esters, hydroxy \*\*\*thiol\*\*\* containing esters, cross-linked \*\*\*thiol\*\*\* ester, unsaturated esters and epoxidized unsaturated esters are measured particular analytical techniques. \*\*\*Thiol\*\*\* sulfur values were obtained using a silver nitrate titration as described in ASTM D3227 or by Raman spectroscopy. Carbon-carbon double bond to \*\*\*thiol\*\*\* group molar ratio, cyclic sulfide to \*\*\*thiol\*\*\* group molar ratios were determined by .sup.13C NMR and/or GC analysis of the \*\*\*thiol\*\*\* containing ester or hydroxy \*\*\*thiol\*\*\* containing ester side chains.

DETD \*\*\*Thiol\*\*\* Sulfur Content by Raman Spectroscopy

DETD \*\*\*Thiol\*\*\* sulfur content was measured by both silver

nitrate  
titration, ASTM D3227, and/or Raman spectroscopy. The Raman spectroscopy method is practiced by measuring the Raman spectra of the \*\*\*thiol\*\*\* containing ester, hydroxy \*\*\*thiol\*\*\* containing ester, cross-linked \*\*\*thiol\*\*\* ester and comparing the spectra to calibration standards containing know \*\*\*thiol\*\*\* compounds having know amounts of \*\*\*thiol\*\*\* groups. Generally, the calibration standard \*\*\*thiol\*\*\* compound has a similar structure to the \*\*\*thiol\*\*\* containing esters analyzed.

DETD The \*\*\*thiol\*\*\* containing esters, hydroxy \*\*\*thiol\*\*\* containing esters and cross-linked \*\*\*thiol\*\*\* ester \*\*\*thiol\*\*\* content were determined by comparing the Raman spectra of the \*\*\*thiol\*\*\* containing esters, hydroxy \*\*\*thiol\*\*\* containing esters and cross-linked \*\*\*thiol\*\*\* ester to calibration standards prepared from mercaptanized methyl oleate diluted in soybean oil to known \*\*\*thiol\*\*\* sulfur contents. \*\*\*Thiol\*\*\* sulfur calibration standards were prepared using standards using various known concentration of mercaptanized methyl oleate diluted in soybean oil.

DETD Raman spectra of the calibration standards and the \*\*\*thiol\*\*\* containing esters, hydroxy \*\*\*thiol\*\*\* containing esters and cross-linked \*\*\*thiol\*\*\* ester were measured using a Kaiser Hololab 5000 Process Raman spectrometer, using a 785 nm laser. \*\*\*Thiol\*\*\* containing esters, hydroxy \*\*\*thiol\*\*\* containing esters and cross-linked \*\*\*thiol\*\*\* ester samples and the \*\*\*thiol\*\*\* sulfur calibration standard Raman spectra were obtained by collecting four 10 second scans which were then processed using Holoreact software. \*\*\*Thiol\*\*\* sulfur values for the \*\*\*thiol\*\*\* containing esters, hydroxy \*\*\*thiol\*\*\* containing esters and cross-linked \*\*\*thiol\*\*\* ester were then calculated using the ratio of the peak area values of the \*\*\*thiol\*\*\* SH peak (center: 2575 cm-1; area 2500-2650 cm-1), and the C.dbd.O peak (center--1745 cm-1; area--1700-1800 cm-1) and comparing them to the peak area values for the calibration standards and interpolating the containing esters, hydroxy \*\*\*thiol\*\*\* containing esters and cross-linked \*\*\*thiol\*\*\* ester \*\*\*thiol\*\*\* sulfur contents. Repeatability of the \*\*\*thiol\*\*\* sulfur values as measured

by Raman spectroscopy have been shown to have a standard deviation of 0.05-0.1 and a % RSD of 0.6-1.5 using 5 samples having a % sulfur content ranging from 3.1-10.6 weight percent as measured over a two month period.

DETD The Raman spectroscopy technique for determining the sulfur content of a containing ester, hydroxy containing ester, and a cross-linked containing ester has been illustrated using a containing ester produced from soybean oil. However, one skilled in the art may adapt and apply the Raman spectroscopy technique for determining the sulfur content of other containing esters, hydroxy containing esters, and a cross-linked containing esters described herein.

DETD C.dbd.C to Thiol Group and Cyclic Sulfide Group to Tool Group

Molar Ratios by <sup>13</sup>C NMR

DETD Carbon-carbon double bond to group molar ratio and cyclic sulfide group to group molar ratios were determined by <sup>13</sup>C NMR. containing ester

<sup>13</sup>C NMR spectra were obtained on a Varian Mercury INOVA400 NMR, a Varian Mercury Plus 300 NMR, or equivalent spectrometer (75.5 MHz <sup>13</sup>C NMR). Peak areas were determined for the cyclic sulfide carbon atoms, group HS--C carbon atoms and carbon-carbon double bonds carbon atoms using the <sup>13</sup>C NMR regions indicated in the table below:

Functional Group	<sup>13</sup> C NMR Region	Number of Carbon Atoms/Group
Cyclic Sulfide Carbon Atoms	49-49.5 ppm	2
HS--C Carbon Atoms	40-41.5 ppm	1
C.dbd.C Carbon Atoms	120-140 ppm	2

DETD The containing ester cyclic sulfide to group molar ratio were calculated by dividing the cyclic sulfide carbon atoms <sup>13</sup>C NMR peak area by 2 (to account for the 2 carbon atoms per cyclic sulfide group) and dividing the resultant number by the group HS--C carbon atoms <sup>13</sup>C NMR peak area.

The containing ester carbon-carbon double bond to group molar ratio were calculated by dividing the

C.dbd.C  
carbon atoms .sup.13C NMR peak area by 2 (to account for the 2  
carbon  
atoms per carbon-carbon double bond) and dividing the result  
number by  
the \*\*\*thiol\*\*\* group HS--C carbon atoms .sup.13C NMR peak  
area  
Offset sample .sup.13C NMR's for soybean oil and a \*\*\*thiol\*\*\*  
containing ester produced from soybean oil using the disclosed  
process  
is provided as FIG. 1.  
DETD The NMR technique for analyzing the unsaturated ester and the  
\*\*\*thiol\*\*\* containing ester produced from an unsaturated  
ester have  
been illustrated using .sup.13C NMR on soybean oil the  
\*\*\*thiol\*\*\*  
containing ester produced from soybean oil. However, one skilled  
in the  
art may adapt and apply either the .sup.13C NMR or .sup.1H NMR  
technique  
to analyze the unsaturated esters and \*\*\*thiol\*\*\* containing  
ester  
produced from the unsaturated ester described herein.  
DETD \*\*\*Epoxide\*\*\* Group to \*\*\*Thiol\*\*\* Group Molar Ratios by  
.sup.13C or .sup.1H NMR  
DETD The \*\*\*epoxide\*\*\* group to \*\*\*thiol\*\*\* group molar  
ratios were  
determined using .sup.1H or .sup.13C NMR. Hydroxy \*\*\*thiol\*\*\*  
containing ester .sup.1H or .sup.13C NMR spectra were obtained on  
a  
Varian Mercury INOVA400 NMR, a Varian Mercury Plus 300 NMR, or  
equivalent spectrometer (300 MHz .sup.1H NMR-75.5 MHz .sup.13C  
NMR).  
Peak areas were determined for the \*\*\*epoxide\*\*\* group and  
sulfide  
group using the .sup.13C and or .sup.1H regions indicated in the  
table  
below:

Functional Group	<sup>1</sup> H NMR Region	<sup>13</sup> C NMR Region	Number of Carbon Atoms/Group	Number of Hydrogen Atoms/Group
***Epoxide*** 2 Carbon Atoms	Group	2.75–3.2 ppm	53.6–56.6 ppm	2
HS–C Carbon Atoms	3.2–4 ppm	40–41.5 ppm	1	1
DETD group to	The hydroxy	***thiol***	containing ester	***epoxide***
(to	***thiol***	group molar ratio were calculated by dividing the		
group	***epoxide***	group carbon atoms <sup>1</sup> H NMR peak area by 2		
the	account for the 2 hydrogen atoms attached to the ***epoxide***			
	carbon atoms) and dividing the result number by the ***thiol***			
	group HS–C carbon atom hydrogens <sup>13</sup> C NMR peak area. Similarly,			

hydroxy \*\*\*thiol\*\*\* containing ester \*\*\*epoxide\*\*\* group  
to  
\*\*\*thiol\*\*\* group molar ratio were calculated using <sup>13</sup>H NMR  
peak  
areas.  
DETD The average number of \*\*\*epoxide\*\*\* group per epoxidized  
unsaturated ester molecule can be determined utilizing similar  
methods  
utilizing either the carbonyl group carbon atom or the C--O ester  
group  
carbon atoms <sup>13</sup>C NMR peak areas in conjunction with the  
\*\*\*epoxide\*\*\* group <sup>13</sup>C NMR peak area. Sample <sup>1</sup>H  
NMR's  
epoxidized soybean oil and a \*\*\*thiol\*\*\* containing ester  
produced  
from epoxidized soybean oil 1 are provided in FIG. 2.  
DETD The NMR technique for analyzing the epoxidized unsaturated ester  
and  
the \*\*\*thiol\*\*\* containing ester produced from an epoxidized  
unsaturated ester (a hydroxy \*\*\*thiol\*\*\* containing ester)  
has been  
illustrated using <sup>1</sup>H NMR on epoxidized soybean oil the  
\*\*\*thiol\*\*\* containing ester produced from epoxidized soybean  
oil.  
However, one skilled in the art may adapt and apply either the  
<sup>1</sup>H  
NMR or <sup>13</sup>C NMR technique to analyze the epoxidized  
unsaturated  
esters and \*\*\*thiol\*\*\* containing ester produced from the  
epoxidized  
unsaturated ester described herein.  
DETD Analysis of Unsaturated Esters, Epoxidized Unsaturated Esters,  
\*\*\*Thiol\*\*\* Containing Esters, and Hydroxy \*\*\*Thiol\*\*\*  
Containing  
Esters by Methanolysis  
DETD Many properties of the unsaturated esters, epoxidized  
unsaturated  
esters, \*\*\*thiol\*\*\* containing esters, and hydroxy  
\*\*\*thiol\*\*\*  
containing ester were and/or can be determined by converting the  
complex  
ester molecules into their component polyols and carboxylic acid  
methyl  
esters. The converted esters are then analyzed by gas  
chromatography  
(GC) and/or gas chromatography/mass spectrometry (GCMS) to  
determine the  
composition of the complex ester side chains. Properties that are  
or can  
be determined by the methanolysis followed by GC or GC/MS of the  
carboxylic acid methyl esters include the number of side chain  
that  
contain \*\*\*thiol\*\*\* groups, the percent of \*\*\*thiol\*\*\*  
group  
sulfur, the number of (or average number) of double bonds per  
ester  
molecule, the molecular weight distribution (or average molecular  
weight) of the ester side chains, The number of (or average  
number of)  
\*\*\*epoxide\*\*\* groups per ester molecule, the cyclic sulfide



to  
to  
group to  
\*\*\*\*thiol\*\*\* group molar ratio, the carbon-carbon double bond  
\*\*\*\*thiol\*\*\* group molar ratio, and the \*\*\*epoxide\*\*\*  
\*\*\*\*thiol\*\*\* group molar ratio, among others.

DETD Depending upon the material being subjected to the methanolysis procedure, there are two methanolysis procedures that were practiced upon the unsaturated ester, epoxidized esters, \*\*\*\*thiol\*\*\* containing ester, and hydroxy \*\*\*\*thiol\*\*\* containing esters described within the experimental section.

DETD Unsaturated esters and \*\*\*\*thiol\*\*\* containing ester produced from unsaturated ester were subjected to a hydrogen chloride based methanolysis procedure. In the hydrogen chloride methanolysis procedure, a 50 to 100 mg sample of the \*\*\*\*thiol\*\*\* containing ester is contacted with 3 mL of 3 N methanolic HCl and reacted for 2 hours a 50.degree. C. The solution is then allowed to cool and the neutralized with a dilute sodium bicarbonate solution. The solution's organic components are then extracted with ethyl ether and analyzed by GC and/or GC/MS. Additional details for the methanolic hydrogen chloride methanolysis procedure may be found in the product specification sheet for methanolic HCl, 0.5 N and 3 N as supplied by Supelco.

DETD Epoxidized unsaturated esters and hydroxy \*\*\*\*thiol\*\*\* containing esters produced from epoxidized unsaturated esters were subjected to a sodium methoxide based methanolysis procedure. The sodium methoxide methanolysis procedure was based upon the procedure disclosed in U.S. Pat. No. 3,991,089. In the sodium methoxide methanolysis procedure, approximately 1 g of the ester was placed in a 50 mL vial with 5.0 mL 25% sodium methoxide in methanol, and 10 mL methanol. The mixture was shaken for approximately 1 hour at room temperature, during which time the solution became one phase. The mixture was then poured into 25 mL of distilled water. Diethyl ether, 25 mL, was added to the solution and the mixture was acidified with 0.5 N HCL to a pH of approximately 5. The organic layer was separated from the aqueous layer using a separatory funnel. The organic layer was washed successively with distilled water (15 mL) and brine solution (15 mL) and then dried over magnesium sulfate. The magnesium sulfate was separated from the organic solution by filtration and the solvent removed by rotary evaporation.

DETD FIG. 3 provides a GC/MS trace of a mercaptanized soybean oil

subjected

to the methanolysis procedure and analyzed by GC/MS using a HP-5  
30

m.times.0.32 mm id.times.0.25 .mu.m film thickness GC Column.

Table 11

provides the GC/MS trace peak assignments.

TABLE 11

GC/MS Data for Methanolysis of A \*\*\*Thiol\*\*\* Containing Ester  
Produced from  
Soybean Oil

GC Retention time Methyl Ester Carboxylic Acid Assignment

21.58	Methyl hexadecanoate
23.66	Methyl (C18 monoene)oate
23.74	Methyl (C18 monoene)oate
23.96	Methyl octadecanoate
26.46	Methyl (C18 Monoene monomercaptan)oate
26.59	Methyl (C18 Monoene monomercaptan)oate
26.66	Methyl (C18 Monoene monomercaptan)oate
26.80	Methyl (C18 monomercaptan)oate
27.31	Methyl (C18 cyclic sulfide)oate
27.44	Methyl (C18 cyclic sulfide)oate
29.04	Methyl (C18 dimercaptan)oate
29.15	Methyl (C18 dimercaptan)oate
29.37	Methyl (C18 monoene dimercaptan)oate
29.46	Methyl (C18 monoene dimercaptan)oate
30.50	Methyl (C18 di (cyclic sulfide))oate

Peaks at 29.37 or 29.46 could also contain Methyl (C18 cyclic sulfide  
monomercaptan)oate isomers as part of those peaks.

DETD FIG. 5 provides a GC/MS trace of an epoxidized soybean oil  
contacted

with hydrogen sulfide (a hydroxy \*\*\*thiol\*\*\* containing  
ester)

subjected to the methanolysis procedure and analyzed by GC/MS  
using a

HP-5 30 m.times.0.32 mm id.times.0.25 .mu.m film thickness GC  
Column.

Table 13 provides the GC/MS trace peak assignments.

TABLE 13

GC/MS Data for Methanolysis of a Hydroxy \*\*\*Thiol\*\*\* Containing  
Ester

Produced from Epoxidized Soybean Oil

GC

Retention

time Methyl Ester Carboxylic Acid Assignment

16.09	Methyl hexadecanoate
17.68	Methyl octadecanoate
18.94	Methyl (C18 monoepoxide)oate
19.94	Methyl (C18 diepoxide)oate
20.14	Methyl (C18 diepoxide)oate
20.75	Methyl (C18 monohydroxy monothiol)oate
21-21.5	Methyl (C18 triepoxide)oate
22.82	Methyl (C18 dihydroxy dithiol)oate
22.90	Methyl (C18 monoepoxide monohydroxy monothiol)oate

27-27.5 Unidentified mixture of C18 sulfur containing methyl esters

DETD The methanolysis procedure and GC/MS procedure has been illustrate using soybean oil, epoxidized soybean oil, and the \*\*\*thiol\*\*\* containing products derived from soybean oil and epoxidized soybean oil.

However, one skilled in the art can easily adapt the procedures to the analysis of other unsaturated esters, epoxidized unsaturated ester, and the \*\*\*thiol\*\*\* containing products derived from the unsaturated esters and epoxidized unsaturated esters as described herein.

DETD The polythiourethane produced from the \*\*\*thiol\*\*\* containing esters, hydroxy \*\*\*thiol\*\*\* containing esters, and cross linked \*\*\*thiol\*\*\* containing ester were analyzed using ASTM E1545-95A and E228-95 to provide the glass transition temperatures and the coefficients of thermal expansion. Shore hardness of the polythiourethanes were determined using ASTM D2240-02A. The polythiourethane were also subject to a subjective analysis classifying the polythiourethanes as hard, flexible, rubbery, rigid, tough, brittle, and other characteristics.

CLM What is claimed is:

1. A cross-linked \*\*\*thiol\*\*\* ester composition comprising \*\*\*thiol\*\*\* ester oligomers having at least two \*\*\*thiol\*\*\* ester monomers connected by a polysulfide linkage having a structure --S.sub.Q--, wherein Q is greater than 1.

CLM What is claimed is:

2. The cross-linked \*\*\*thiol\*\*\* ester composition of claim 1, wherein the \*\*\*thiol\*\*\* ester oligomers have at least three \*\*\*thiol\*\*\* ester monomers connected by polysulfide linkages.

CLM What is claimed is:

3. The cross-linked \*\*\*thiol\*\*\* ester composition of claim 1, wherein the \*\*\*thiol\*\*\* ester oligomers have from 3 to 20 \*\*\*thiol\*\*\* ester monomers connected by polysulfide linkages.

CLM What is claimed is:

4. The cross-linked \*\*\*thiol\*\*\* ester composition of claim 1, wherein the crosslinked \*\*\*thiol\*\*\* ester composition comprises \*\*\*thiol\*\*\* ester monomers and \*\*\*thiol\*\*\* ester oligomers.

CLM What is claimed is:

5. The cross-linked \*\*\*thiol\*\*\* ester composition of claim 4, wherein the \*\*\*thiol\*\*\* ester monomers and \*\*\*thiol\*\*\* ester oligomers have a total \*\*\*thiol\*\*\* sulfur content from 0.5 to 8 weight percent.

CLM     What is claimed is:  
6. The cross-linked     \*\*\*thiol\*\*\*     ester composition of claim 4,  
wherein the combined     \*\*\*thiol\*\*\*     ester monomers and  
\*\*\*thiol\*\*\*  
ester oligomers have an average molecular weight greater than  
2000.

CLM     What is claimed is:  
7. The cross-linked     \*\*\*thiol\*\*\*     ester composition of claim 4,  
wherein the     \*\*\*thiol\*\*\*     ester monomers and     \*\*\*thiol\*\*\*  
ester  
oligomers have an average molecular weight from 2000 to 20,000.

CLM     What is claimed is:  
8. The cross-linked     \*\*\*thiol\*\*\*     ester composition of claim 4,  
wherein the     \*\*\*thiol\*\*\*     ester monomers and     \*\*\*thiol\*\*\*  
ester  
oligomers have a total sulfur content ranging from 8 to 15 weight  
percent.

CLM     What is claimed is:  
9. A cross-linked     \*\*\*thiol\*\*\*     ester composition produced by  
the  
process comprising the steps of: a) contacting a     \*\*\*thiol\*\*\*  
ester  
composition with an oxidizing agent; and b) reacting the  
\*\*\*thiol\*\*\*  
ester and the oxidizing agent to form     \*\*\*thiol\*\*\*     ester  
oligomers  
having at least two     \*\*\*thiol\*\*\*     ester monomers connected by a  
polysulfide linkage having a structure --S.sub.Q--, wherein Q is  
greater  
than 1.

CLM     What is claimed is:  
10. A process to produce a cross-linked     \*\*\*thiol\*\*\*     ester  
composition comprising: a) contacting a     \*\*\*thiol\*\*\*     ester  
composition with an oxidizing agent; and b) reacting the  
\*\*\*thiol\*\*\*  
ester and the oxidizing agent to form     \*\*\*thiol\*\*\*     ester  
oligomers  
having at least two     \*\*\*thiol\*\*\*     ester monomers connected by a  
polysulfide linkage having a structure --S.sub.Q--, wherein Q is  
greater  
than 1.

CLM     What is claimed is:  
13. The process of claim 10, wherein the     \*\*\*thiol\*\*\*     ester is  
a  
hydroxy     \*\*\*thiol\*\*\*     ester.

CLM     What is claimed is:  
14. The process of claim 10, wherein a weight ratio of elemental  
sulfur  
to     \*\*\*thiol\*\*\*     sulfur in the     \*\*\*thiol\*\*\*     ester molecules  
ranges  
from 0.5 to 32.

CLM     What is claimed is:  
15. The process of claim 10, wherein step of the reacting the

\*\*\*thiol\*\*\* ester and the oxidizing agent is performed at a temperature ranging from 25.degree. C. to 150.degree. C.

CLM What is claimed is:  
16. The process of claim 10, wherein residual hydrogen sulfide is stripped from the cross-linked \*\*\*thiol\*\*\* ester composition produced.

CLM What is claimed is:  
17. The process of claim 12, wherein the reaction of the \*\*\*thiol\*\*\* ester and the elemental sulfur is catalyzed.

IT 102-85-2, Tri-n-butylphosphite \*\*\*6674-22-2\*\*\* ,  
1,8-Diazabicyclo[5.4.0]undec-7-ene  
(activator; thiol ester compns. prepd. by reacting H2S with unsatd.

esters, such as soybean oil for manuf. monomers for prodn. of polythiourethanes for fertilizers)

ACCESSION NUMBER: 2005:227538 USPATFULL <<LOGINID::20090306>>

TITLE: \*\*\*Thiol\*\*\* ester compositions and processes for

INVENTOR(S): making and using same  
Byers, Jim D., Bartlesville, OK, UNITED STATES  
Refvik, Mitchell D., Bartlesville, OK, UNITED STATES

STATES

PATENT ASSIGNEE(S): Brown, Chad D., Bartlesville, OK, UNITED STATES  
Chevron Phillips Chemical Company LP (U.S. corporation)

	NUMBER	KIND	DATE
PATENT INFORMATION:	US 20050197390	A1	20050908
APPLICATION INFO.:	US 2005-59792	A1	20050217 (11)

	NUMBER	DATE
PRIORITY INFORMATION:	US 2004-545260P	20040217 (60)
	US 2004-561614P	20040413 (60)
	US 2004-561685P	20040413 (60)
	US 2004-561855P	20040413 (60)
DOCUMENT TYPE:	Utility	
FILE SEGMENT:	APPLICATION	
LEGAL REPRESENTATIVE:	CHEVRON PHILLIPS CHEMICAL COMPANY LP, LAW	
DEPARTMENT -	IP, P.O BOX 4910, THE WOODLANDS, TX, 77387-4910,	
US		
NUMBER OF CLAIMS:	18	
EXEMPLARY CLAIM:	1	
NUMBER OF DRAWINGS:	14 Drawing Page(s)	
LINE COUNT:	6310	
CAS INDEXING IS AVAILABLE FOR THIS PATENT.		

=> logoff

ALL L# QUERIES AND ANSWER SETS ARE DELETED AT LOGOFF

LOGOFF? (Y)/N/HOLD:y

COST IN U.S. DOLLARS

SINCE FILE

TOTAL

ENTRY

SESSION

FULL ESTIMATED COST

80.60

110.85

STN INTERNATIONAL LOGOFF AT 15:34:50 ON 06 MAR 2009